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ENVIRONMENTAL RESEARCH

# THE MEASUREMENT OF EMISSIONS FROM LANDFILLS AND NATURAL GAS DISTRIBUTION SYSYTEMS

ERP Project 628C
FINAL REPORT

MINISTRY OF ENVIRONMENT AND ENERGY

Ontario

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# FINAL REPORT

# THE MEASUREMENT OF EMISSIONS FROM LANDFILLS AND NATURAL GAS DISTRIBUTION SYSTEMS

Submitted by

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*ENVIRONMENTAL MONITORING SYSTEMS AND MEASUREMENTS*

Final Report to
Ontario Ministry of Environment and Energy
in completion of contract
under
RAC Project no. 628C

**DISCLAIMER**

The statements and conclusions in this report are those of Unisearch Associates Inc. and not necessarily those of Ontario Ministry of Environment and Energy and Consumers Gas. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

**ACKNOWLEDGMENTS**

We wish to thank the staff of the Keele Valley Landfill, especially Martin Edlenbos and Tad Lipowicz, for their valuable assistance during the field measurement program at their location. We wish to also thank Dr. Diane Michelangeli and Ms. Jennifer Kirkaldy both from Senes Consultants for running the models and preparing the contour plots included in this report. We are grateful to OMEE RAC Project 628C and Consumers Gas Project ER1557 for their financial support throughout this project.

## EXECUTIVE SUMMARY

Under joint contract to OMEE and Consumers Gas, Unisearch Associates Inc. applied the TDLAS (Tunable Diode Laser) technology to make measurements of $CH_4$ (methane) and $C_2H_6$ (ethane). These measurements were taken at the Keele Valley Landfill, The Maple TransCanada Pipelines Compressor Station and various urban, industrial and rural sites around Toronto. The work consisted in 1)developing the EMS-50 system to measure these two species simultaneously, this was done by selecting appropriate lasers where the wavelength region identified contained adjacent absorption features for $CH_4$ and $C_2H_6$, 2)conducting laboratory studies to optimize the detection limits and response time of these two species, , 3)conducting measurements around various land types which necessitated the building of a mobile laboratory for the inclusion of the EMS-50, the integration of a meteorological station and Global Positioning Station (GPS), 4)optimizing the experimental technology to do detailed mapping of the Keele Valley Landfill so $CH_4$ flux emissions could be determined, 5)investigate the methane/ethane ratio to see if leak determination from natural gas pipelines is feasible using this technology, 6)using the database from (4) and (5), do model runs to see how they would compare to actual ambient and flux chamber measurements, 7)using results from the models give estimations of $CH_4$ emissions from the two primary investigative sites. Since methane is a greenhouse gas, this project was undertaken in a hope to better estimate its emission from the sources investigated. The methodology developed will ultimately be used to look at the contribution to global warming from these sources.

The results of the work as well as plans for the next steps were submitted on an ongoing basis in 23 progress reports during the course of this project. A major first year interim report was submitted with progress report 12 summing the first years work. The interim report has been included as subsection 2 in the final report for completeness.

Laboratory experiments indicated that lasers were available where the absorption lines for both methane and ethane are in close proximity to allow simultaneous measurements. These lasers were characterized in the lab and with improvements to line fitting of the ambient spectra to the calibration spectra detection limits were determined to be about 4 ppbv for $CH_4$ and 10 ppbv for $C_2H_6$. These detection limits are for an instrument with a response of 0.1 second and improve with longer integration times.

Field measurements were made at residential, rural and industrial land use sites to make a qualitative evaluation of the $CH_4$ emissions at these locations. Results indicate that their methane contributions are quite small.

Field measurements were made at the TCPL compressor station in Maple, Ontario over four sampling days. Perimeter runs around this station indicated levels of higher than background emissions with a possible contribution of between 1 to 2 g/s of methane emitting from the source. These levels are overall still quite low and during the measurement program we were unable to confirm the type of source (natural gas or other methane emitters) by the measurement of ethane. Ethane emissions were below the 10 ppbV detection limit the entire time around the TCPL station.

Ambient measurements were made at the Keele Valley Landfill to permit two entire mappings over the landfill surface at two heights. The heights being 10cm and 1 meter above the surface. A combination of geopositional data as well as ambient data was used in making a surface plot of this landfill for October 6, 1994. This plot showed four distinct locations of higher emissions over the landfill. Flux chamber measurements according to the prescribed EPA method were made to compare surface flux measurements with ambient measurements. The results clearly showed that the flux chamber methodology is much more expensive to conduct, more time consuming and underestimated the total $CH_4$ emissions by at least a factor of 6. The flux chamber methodology only provides a good tool to evaluate soil cover efficiency.

The ambient measurements over the landfill provided methodology to include fugitive (point or area) sources into the total emissions. Total emissions from the Keele Valley Landfill were estimated from the ambient measurements (perimeter run data) to be 11.5 g/s. Emissions from the flux chamber method alone were under 2 g/s. Landfill emissions from the detailed mappings have yet to be analyzed to the extent necessary for flux emissions but clearly show a strong gradient between the two heights measured. This existing data set with further analysis would be a valuable tool in developing and validating existing models.

Contour plots of the data sets were made and compared with the Fugitive Dust Model (FDM). Results showed that by including only flux chamber measurements with corresponding meteorological data the FDM and ambient measurements were not in agreement but when likely point and area sources were included into the model, as indicated from the surface mapping, the FDM was in much better agreement with the ambient measurements.

The TDLAS methodology as applied to the measurement of ambient $CH_4$ at both a landfill and a natural gas distribution center has shown that it is a highly sensitive technique as good or better than any other available. It provides high spectral resolution and absolute identification of methane and ethane. With response times of 0.1 seconds provides a technique for specific real time measurements of $CH_4$ and $C_2H_6$. The very high quality data this technique provides will permit significant insight into the emissions from the sources measured.

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# ASSESSMENT METHODOLOGIES FOR GAS EMISSION AND DISPERSION FROM LANDFILLS AND NATURAL GAS DISTRIBUTION CENTERS

## 1.0 INTRODUCTION

This final report is to describe the application of Tunable diode laser (TDLAS) technology to the measurement of methane ($CH_4$) emissions from both landfills and natural gas distribution centers under joint contracts between OME (RAC Project No. 628C/ Agreement No. A32499-00) and Consumers Gas (Project No. ER1557) with Unisearch Associates Inc. This methodology was developed during the first year of the project and provided satisfactory results on preliminary runs conducted during that initial year. The interim report which summarized the first years effort has been included in this final report in the year one subsection for completeness. We were also able to demonstrate in the lab that we can detect the methane/ethane ratio for natural gas emissions. The second year effort comprised of the field measurement program utilizing this technology. During this period we showed that using real time ambient measurements a landfill can be successfully mapped for $CH_4$ emissions. At this time we have completed three perimeter runs around the Maple TransCanada PipeLines compressor station and although we were able to measure higher than background methane emissions no leaks were detected as ethane levels remained below the 10 ppbv detection limit. From the landfill mapping:

- Hot spots can be identified
- Total $CH_4$ flux can be modeled
- Efficiency of the $CH_4$ recovery system can be assessed

The ultimate goal of this project was to demonstrate that the TDLAS can be an efficient and cost effective monitoring procedure for $CH_4$ emissions. The $CH_4$ data that the TDLAS provides can be used to assess Ontario's contribution to global warming from these two sources.

## 1.1 Background and Rationale

Gas generation in waste landfills emerges from biological processes, volatility of the gas and inherent chemical reactions. Control of these emissions has previously been focused on the explosive hazards due to methane migration and accumulation and/or nuisance due to the odorous trace compounds that lead to justifiable complaints from residents in close proximity to the landfill. Recently concern has been expressed regarding the impact that $CH_4$ emissions contribute to global warming. Methane is an important atmospheric trace gas for many reasons. As a greenhouse gas it is second only to carbon dioxide ($CO_2$) in significance. Methane is a major source of water vapour in the stratosphere and influences stratospheric ozone concentrations. On a global scale $CH_4$ is a major precursor to $O_3$ formation in the troposphere and is a sink for the atmospheres cleansing agent, the hydroxyl radical. Increases in $CH_4$ can therefore have an adverse effect on the atmosphere by reducing its cleansing ability and increasing ground level ozone. Over the last decade it has been increasing at a rate of just less than 1% per year. Estimations of the amount of methane emitted from its major sources, that being from natural wetlands, rice paddies, cattle breeding, biomass burning and coal mining have been found from recent measurements to be lower by a factor between 2 to 4. This suggests either an underestimation of the other sources of methane or an overestimation of the sinks. Landfill and natural gas pipelines are two sources that are gaining increasing attention as an example of a significant source that may have been underestimated. $CH_4$ utilization as an energy source has merit as it reduces atmospheric emissions and may provide a cost effective alternative to passive venting. The composition of landfill gas is highly dependent upon the type of waste disposed. The gas produced by the decomposition of municipal waste is made up of two major components these being methane (approximately 60-65%) and carbon dioxide (about 30-35%) and over 100 trace components]. The rate of waste volatilization is dependent on the physical and chemical properties of the waste and of the adsorbing and absorbing properties of the covering material. The physical environment primarily temperature, wind and pressure affect the evaporation rate of wastes and their subsequent emission

into the atmosphere. This variability surely applies to the emission of $CH_4$ gas and can only be accounted for by real time, "in situ" measurements. The TDLAS method enabled us to conduct real time measurements at any landfill (for this study we chose the Keele Valley Landfill in Maple) or natural gas center location (for this we chose the TransCanada PipeLines compressor station number 130 also in Maple). Methane released from the waste by degradation of the waste or by volatilization of the waste components will migrate vertically out of the filled area or into the soil of adjacent fields. The methane generation may start a few months after the disposal of the waste at the site and may continue for several years. Gas control measures introduced over the years are liners, soil covers, and active extraction of gas and use or treatment before discharge to the atmosphere. The interest in utilization of the landfill gas for energy production has the potential to reduce the problem of landfill gas migration significantly. Natural gas pipelines and their pumping stations are also contributing to atmospheric methane emissions. Since these emissions are highly variable depending on leak rates (etc.) quantification would be quite speculative unless highly specific monitoring methods are utilized.

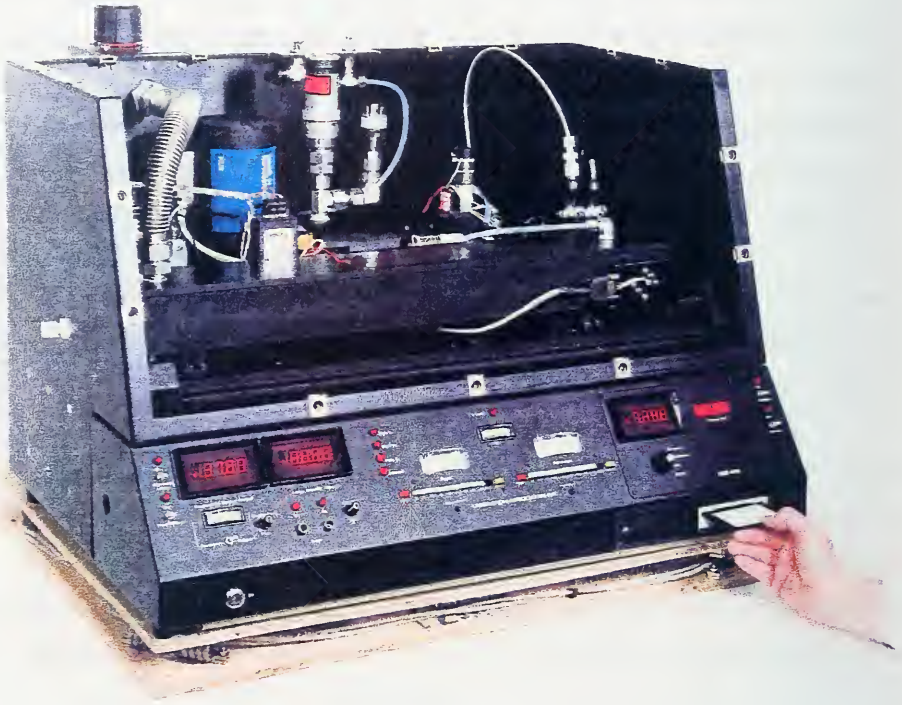
## 2.0 FIRST YEAR EFFORT

### 2.1 Instrumentation

The Unisearch EMS-50 Tunable Diode Laser Absorption spectrometer (TDLAS) was used for the measurement of $CH_4$ and $C_2H_6$. Refer to Photograph 1 which depicts the EMS-50. The TDLAS method is ideally suited for atmospheric $CH_4$ measurements. Its high spectral resolution provides unequivocal identification of $CH_4$, without interference from other gases. Moreover, it can also measure a number of atmospheric gases simultaneously - for example, ethane ($C_2H_6$) and methane. The $C_2H_6$ content of NG is about 1% whereas the atmospheric burden is about 1 ppbv or 0.06%,. Thus the measurement of the methane/ethane ratio provides unequivocal identification of $CH_4$ from a natural gas source. The sensitivity of the TDLAS technique is as good or better than any other available method.

Figure 1 shows a schematic of the EMS-50 optical system. The diode laser is contained in a miniature closed cycle refrigerator which controls the temperature of the diode laser to ± 0.001 K by the use of a heater circuit and a servo temperature controller coupled with the cooling capacity of the refrigerator. The laser emission is collimated by an off-axis parabolic mirror OAP1 and directed by mirror M1 onto OAP2 which focuses the beam onto the entrance of the White cell and the reference detector. A 50:50 beam splitter, BS, divides the laser light so that 1/2 falls on the entrance to the White cell and 1/2 passes through a reference cell containing high concentrations of the target gases, $CH_4$ and $C_2H_6$, and onto the reference detector. Motorized mirrors M2 and M4 are used in conjunction with a two dimensional simplex routine to maintain the alignment on the White cell entrance and reference detector respectively.

# EMS-012 PHOTOGRAPH 1



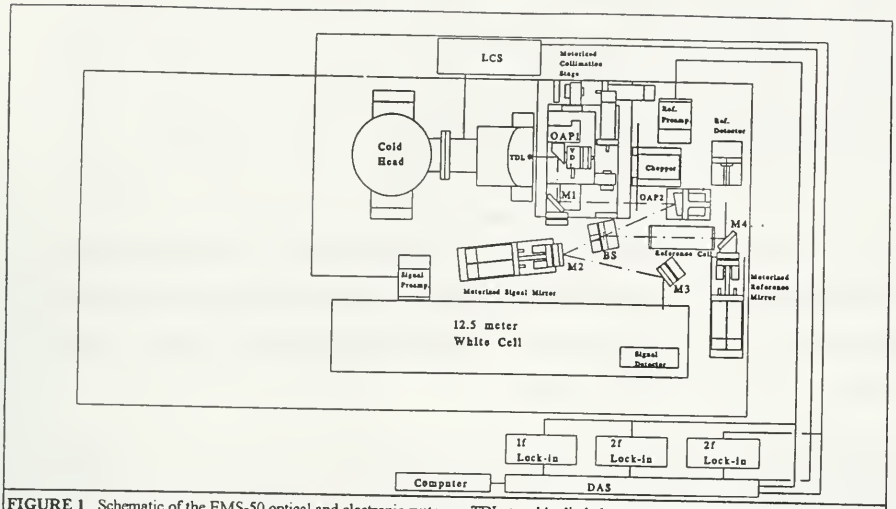



**FIGURE 1**. Schematic of the EMS-50 optical and electronic systems. TDL, tunable diode laser; OAP1-2, off axis parabolic mirrors; VDL, visible diode laser; M1-4, beam directing mirrors; LCS, laser temperature and current control module, DAS, data acquisition system.

Simultaneously with the ambient spectra acquisition, measurements are made on high concentrations of the two target gases which are contained in a short reference cell interposed in the laser beam which is detected at the reference detector. The output of the signal and reference detectors are passed to lock-in amplifiers for processing and then to a data acquisition system/computer for analysis. The ambient signal is least-squares fitted to the reference spectrum in real time to obtain the ambient mixing ratio measurement. Periodic additions of known concentrations of the two gases are added to the White cell to calibrate the reference cells which are then used as transfer standards.

The software was developed to permit continuous, simultaneous measurements on two species, in this case $CH_4$ and $C_2H_6$, at a high data acquisition rate. Employing a 80486DX based computer, data on both species can be acquired at 40 Hz. The computer generates a 128 point voltage ramp which is used to scan the laser current and thereby tune the laser frequency through an absorption feature. Since the ramp source is from a 12 bit A/D board in the computer, the first 64 points of the 4096 point ramp can be selected from the central bits of the A/D and the second 64 points from any other part of the ramp. With a suitable delay of 5-10 milliseconds to allow the laser frequency to stabilize between the two parts of the ramp, a single scan over two frequency regions can be performed in about 0.025 of a second. This permits the measurement of two species, simultaneously with a single Diode Laser.

The raw data is averaged initially into 0.1 second data points which are output to the computer monitor and stored on disk for future analysis if desired. The data is also averaged into a user defined time period which may be chosen to be any period from 1 second to 5 minutes. This is also displayed on the computer screen and may be archived for future analysis at the users discretion.

The power incident on both the reference detector and the signal detector are monitored for each 0.1 second data point and archived along with the mixing ratio measurement. At the users command, the data may be corrected in real time for changes in the ratio of the power measured on each detector. This improves the long term stability of the system. The power measurement also provides a diagnostic for determining when the optical alignment of the system needs correction.

## 2.2 Laboratory Studies

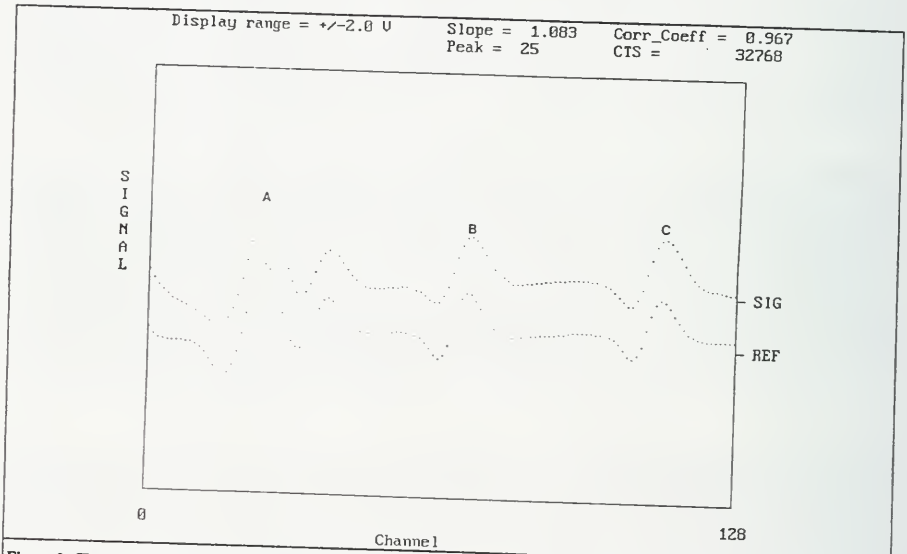
A tunable diode laser capable of measuring both $CH_4$ and $C_2H_6$ simultaneously was procured and installed in the EMS-50 and characterized. Operating conditions where both lines could be monitored simultaneously were identified. Suitable calibrations sources for both gases were acquired and the total system optimized for sensitivity and stability.

Figure 2 shows the 2f spectra of three methane lines at 95 Torr separated by a few tenths of a wavenumber as measured in a single 0.1 second sweep. The top (SIG) trace is for ambient room air in a 12 meter multipass cell, the bottom (REF) trace is for 0.25% methane in a 7.5 cm. reference cell.

Figure 3 illustrates the selection and analysis of the two lines labeled A and C in Figure 2. Notice that the selection is not limited to adjacent lines. The slope and correlation coefficients are for a least squares fit of the SIG to REF spectra performed in real time directly after each scan. The mixing ratio in the absorption cell is proportional to this slope. The slope can be saved to disk and sent to an analog output port giving 0.1 second time resolution of each absorbing species.

By selecting the appropriate wavelength region multiple species can be measured simultaneously. Adjacent absorption features for $CH_4$ and $C_2H_6$ were identified. This allowed simultaneous measurements of $CH_4$ and $C_2H_6$ for the first time.

Figure 4 shows four boxes each containing the 2f spectra of either a methane line (left) or an ethane line (right) at 95 Torr. These lines are separated by a few tenths of a wavenumber as measured in a single 0.1 second sweep shown in the top pair and the accumulated 1 second average signal for both species which is shown in the bottom pair. The top (SIG) trace in each box is ambient room air (which contains ~1.7 ppmv $CH_4$) in a 12 meter multipass cell spiked with 1 ppmv of $C_2H_6$. The bottom (REF) trace is for a ~0.25% methane/ethane mixture in a 7.5 cm. reference cell.

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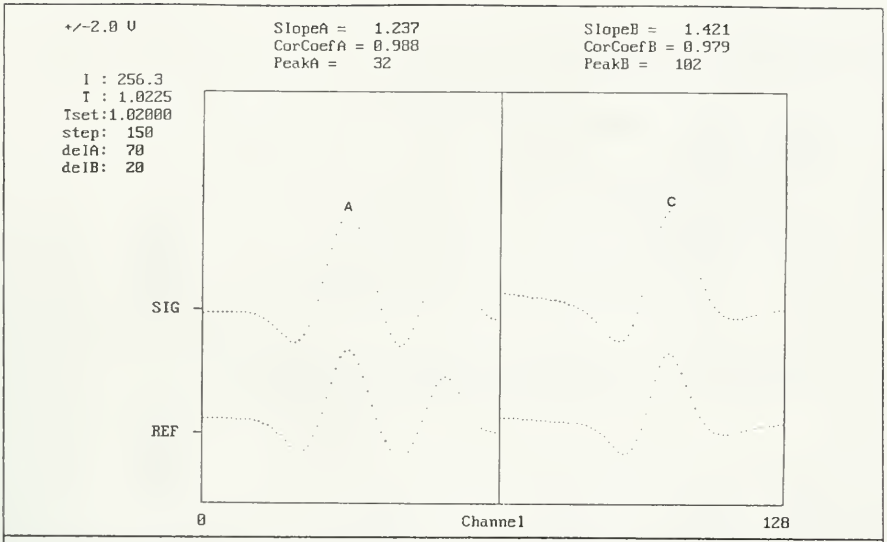



**Figure 3** Two lines labeled A and C in Figure 1 selected for simultaneous analysis.

Figure 5 duplicates the above measurements but with a 250 ppbv spike of ethane. Detection limits for 1 second acquisitions are about 50 ppbv for $C_2H_6$. At 60 km per hr this represents a spatial resolution of ~16 m. Reducing the spatial resolution to 50-100 m provides detection limits of the order of 20 ppbv.

In the laboratory, the long and short term stability of the system when measuring $CH_4$ was found to be typically ± 0.25% (about 4 ppbv) for a 0.1 second integration time. Ethane does not absorb light as strongly as $CH_4$ at 3 microns (where the available lasers emit) and the stability is in the range ± 0.75% (about 10 ppbv). These detection limits are, however, adequate for the proposed measurements as shown in Figure 6 which displays the results obtained for measurements of ambient lab air into which a small spike of natural gas has been introduced.

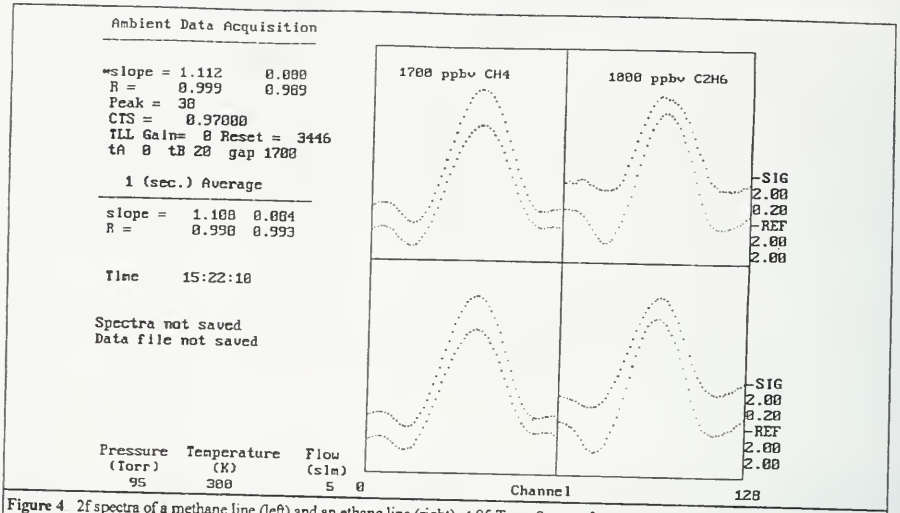



**Figure 4**. 2f spectra of a methane line (left) and an ethane line (right) at 95 Torr. Spectra for a single 0.1 second sweep is shown in the top pair and the accumulated 1 second average signal for both species which is shown in the bottom pair. The top (SIG) trace in each box is ambient room air (which contains ~1.7 ppmv $CH_4$) in a 12 meter multipass cell spiked with 1 ppmv of $C_2H_6$. The bottom (REF) trace is for a ~0.25% methane/ethane mixture in a 7.5 cm. reference cell.

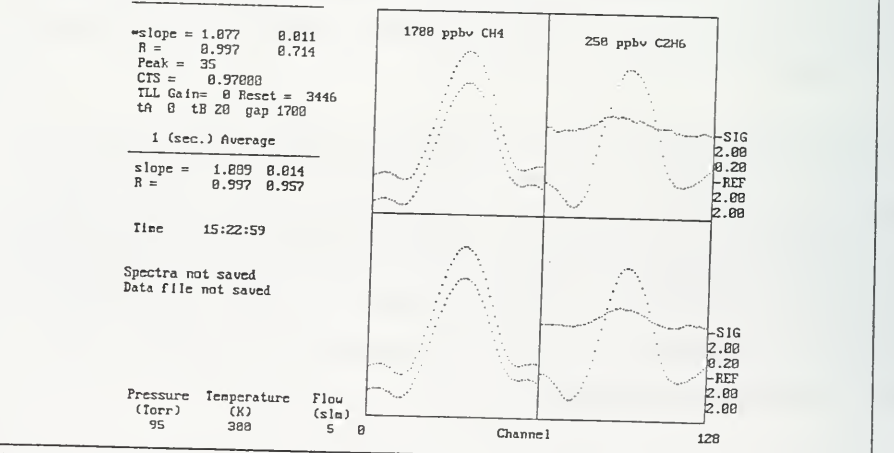



**Figure 5.** 2f spectra of a methane line (left) and an ethane line (right) at 95 Torr. Spectra for a single 0.1 second sweep is shown in the top pair and the accumulated 1 second average signal for both species which is shown in the bottom pair. The top (SIG) trace in each box is ambient room air (which contains ~1.7 ppmv $CH_4$) in a 12 meter multipass cell spiked with 250 ppbv of $C_2H_6$. The bottom (REF) trace is for a ~0.25% methane/ethane mixture in a 7.5 cm. reference cell.

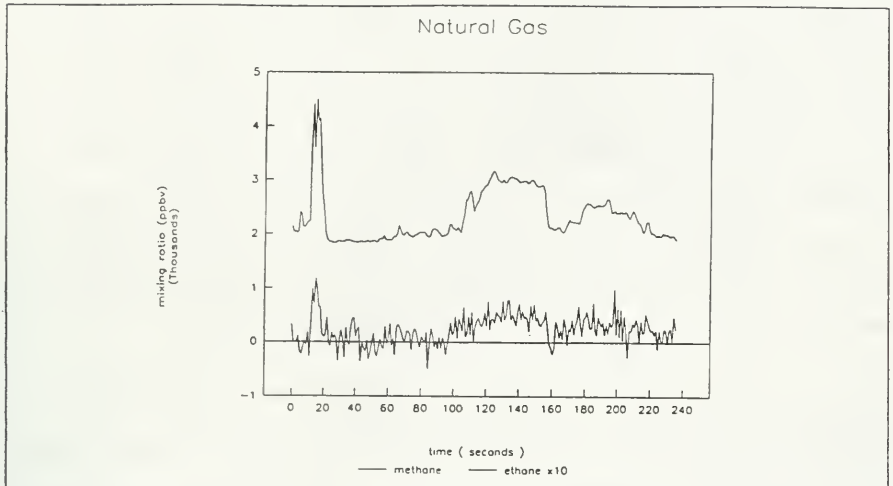



**Figure 6.** Simultaneous measurements of $CH_4$ and $C_2H_6$ in laboratory air when spikes of natural gas are introduced into the sampled air by opening a bottle containing ambient pressure natural gas in the vicinity of the sampling port.

## 2.3 Field Measurements

The TDLAS system was installed in the UNISEARCH mobile laboratory. An initial "shake down" run was done to assess the performance to the instrument. Figure 7 shows a map of the area north of Unisearch and in the vicinity of the Keele Valley Landfill where the first measurements were made. Figure 8 shows the results obtained for measurements of $CH_4$ during the trip. The large increase in $CH_4$ during the time period 50-175 seconds occurred when the mobile lab was located down wind of the landfill. I Figure 7, the numbers printed on the east west road lying to the south of the landfill represent the time in seconds for comparison with the data shown in Figure 8.

As can be seen from the results in Figure 8, the instrument performed very well with little noise evident during non-event periods (times 200-500 seconds).

Measurements were then planned to encompass various types of land use including landfill, Residential and Light industrial. A Global Positioning System was integrated with the laser system to obtain precise positioning information.

Figure 9 shows the route followed for the first measurement run encompassing light industrial (North York between Keele and Alness, north and south of Finch), residential (bounded on the west by Bathurst, east by Bayview, north by Steeles and the south by Sheppard) and landfill site (Keele Valley situated north of Major Mackenzie) land use. Times are indicated on the route map to allow comparison of emissions with the positional information.

Figure 10 shows the $CH_4$ emissions measured over the route depicted in Figure 9. The landfill is the large spike around 20:11 UCT (Universal Coordinated Time, formally GMT). To obtain local time subtract 5 hours. Small increases in $CH_4$ were measured generally at major intersections and probably represent measurements of automobile exhaust. No evidence for major emissions of $CH_4$ from any local sources was observed except in the case of the landfill.

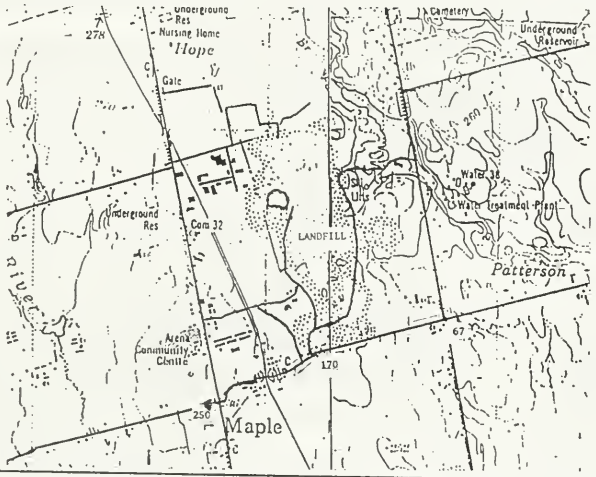



**Figure 7.** Topographical map of the area monitored in the initial "shake down" tests of the EMS-50 for real time measurements of $CH_4$.

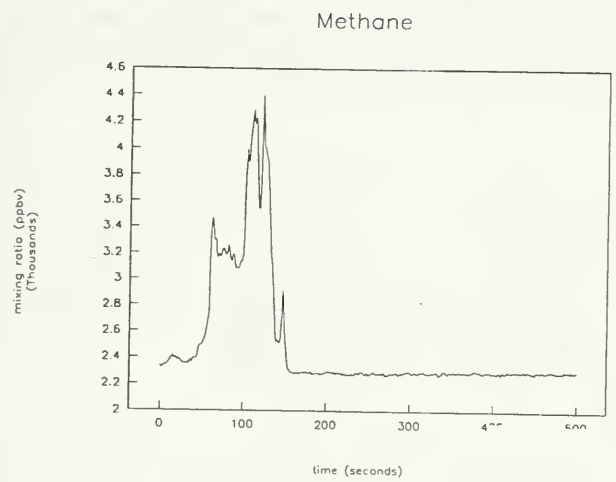



**Figure 8.** Measurements of $CH_4$ obtained during the "shake down" test of the EMS-50 in the region of the Keele Valley Landfill. The large increase in $CH_4$ during times 50-175 seconds occurred when the mobile lab was down wind of the landfill as indicated on Figure 7.

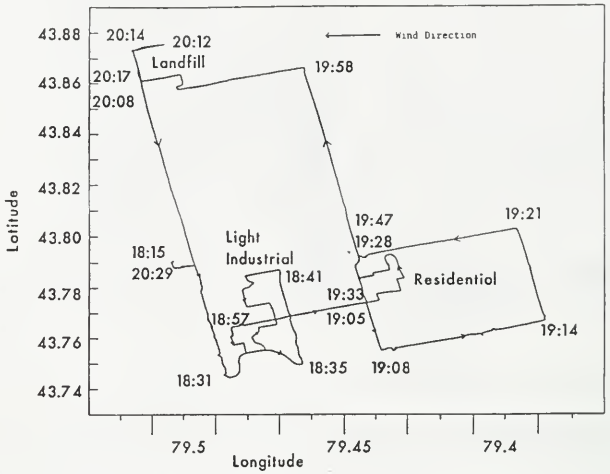



**Figure 9.** Measurement route followed encompassing light Industrial, Residential and landfill land use. The boundaries are: Keele Street on the West, Bayview most easterly, Sheppard to the South and Major Mackenzie to the north. The major north-south road in the middle of the route is Bathurst.

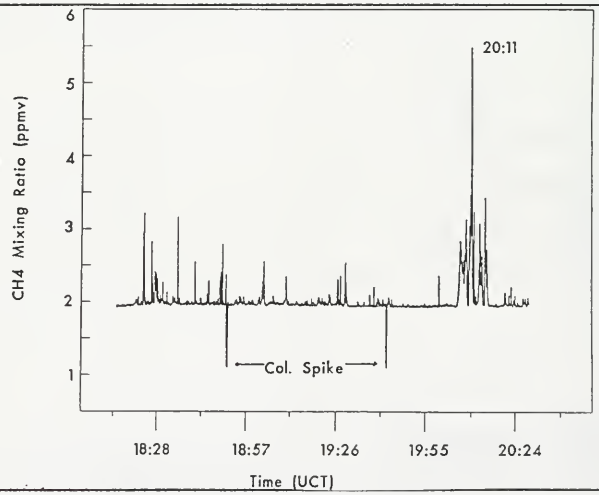



**Figure 10.** Measurements of $CH_4$ obtained during the route depicted in Figure 9 which encompassed light industrial, residential and landfill land use. The majority of the $CH_4$ occurred when the mobile lab was down wind of the landfill as indicated on Figure 9.

The second run included detailed measurements around the Keele Valley Landfill. At this time the ethane measurements commenced. Figure 11 shows the route taken from Unisearch, up Keele street to the landfill and then about the site. Figures 12 and 13 show the results obtained for $CH_4$ and respectively. There was no evidence of $C_2H_6$ emissions at any time in the run. The large peak in the $CH_4$ at the end of the run can be attributed to our own vehicle exhaust which was measured while we were stopped in the Unisearch parking lot.

The third run included detailed measurements around a natural gas distribution site, namely the TransCanada PipeLines compressor station number 130 located just east of Maple, Ontario. Figure 14 shows the route taken for run 3 and Figures 15 and 16 show the results obtained for $CH_4$ and $C_2H_6$ respectively. Only a slight increase in the $CH_4$ emissions were observed when down wind of the compressor station (Figure 17 shows this data in more detail) and there was no evidence for $C_2H_6$. The lack of evidence for $C_2H_6$ emissions is not unexpected considering the very low emissions of $CH_4$ measured at this site. The signal due to $C_2H_6$ would have been below our detection limits in this case.

Several additional measurement runs were made in the Toronto urban area and along the natural gas pipeline during the winter of 1993 with much the same results. Namely, that the landfill was the only significant source of $CH_4$ emissions with automobile exhaust contributing some small events at congested road intersections.

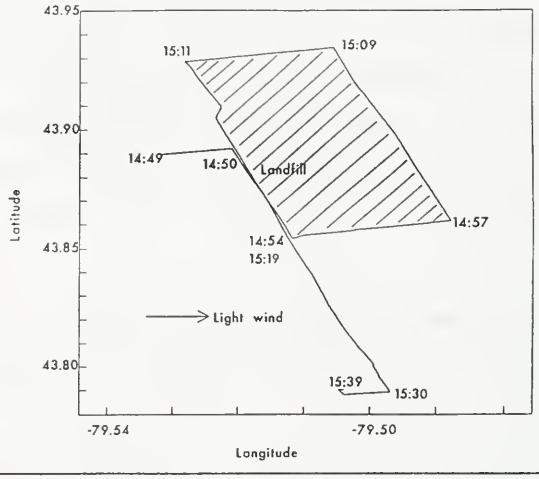



**Figure 11.** Measurement route followed on the second run encompassing the Keele Valley Landfill (shaded area).

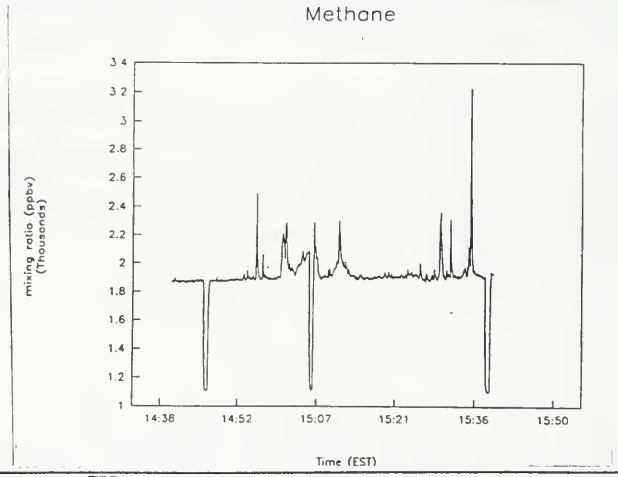



**Figure 12.** Measurements of $CH_4$ obtained during the second run following the route depicted in Figure 11 which encompassed the Keele Valley Landfill. The majority of the $CH_4$ occurred when the mobile lab was down wind of the landfill as indicated on Figure 11. Calibration spikes of 1.1 ppmv $CH_4$ in air were added periodically as indicated to check the stability of the instrument.

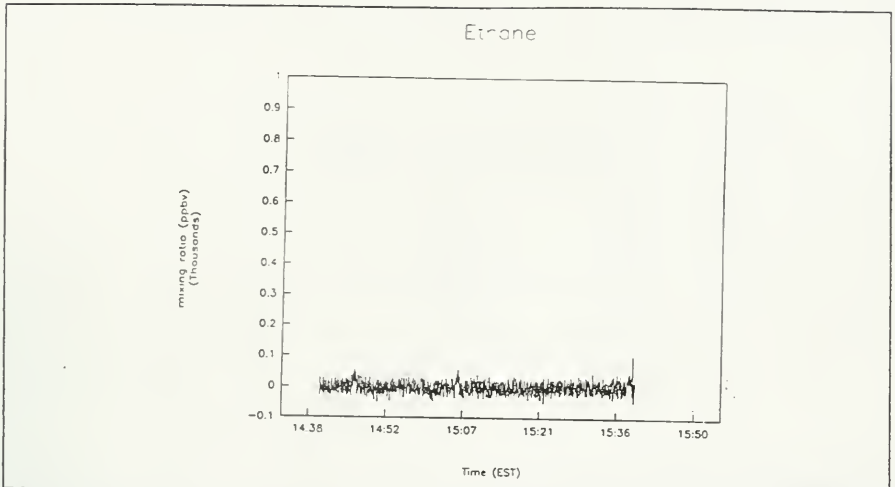



**Figure 13.** Measurements of $C_2H_6$ obtained during the second run following the route depicted in Figure 11 which encompassed the Keele Valley Landfill. There is no evidence for $C_2H_6$ emissions at any time during the run (run average = 0 ± 14 ppbv). The small spikes at 14:45, 15:06 and 15:38 are artifacts of the $CH_4$ calibration performed at these times.

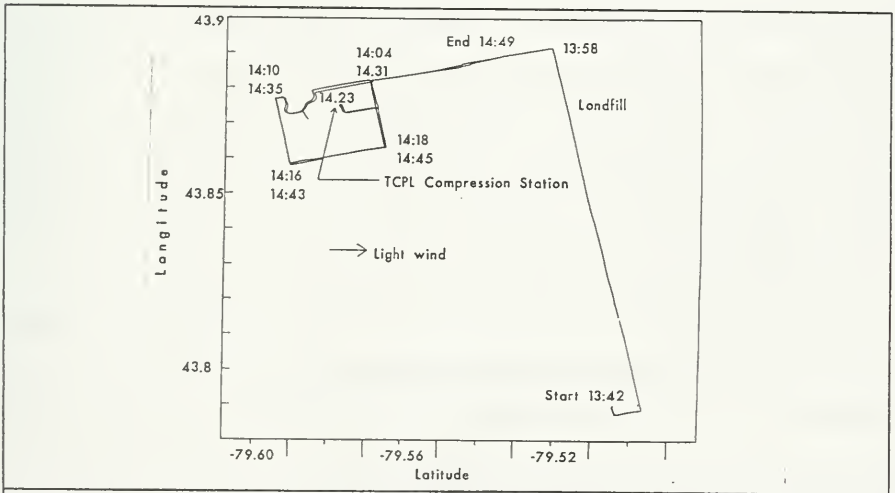



**Figure 14.** Measurement route followed on the third run encompassing the TCPL compressor station at Maple, Ontario.

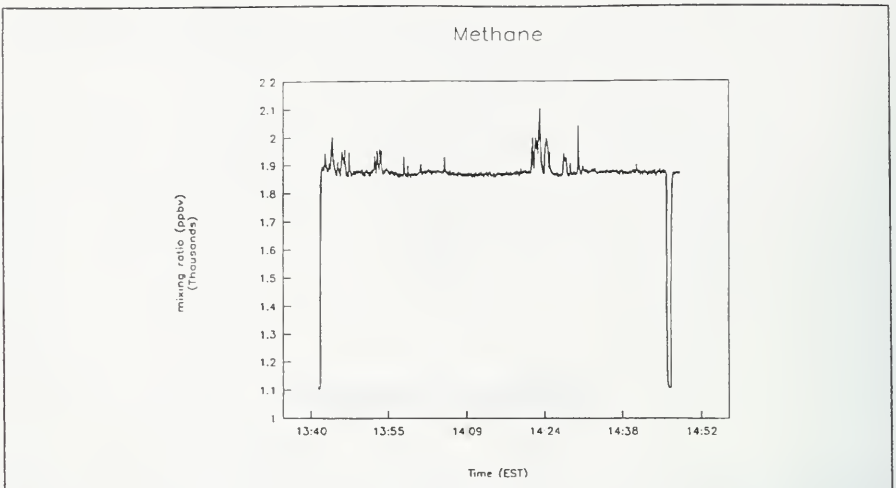



**Figure 15.** Measurements of $CH_4$ obtained during the third run following the route depicted in Figure 14 which encompassed the TCPL compressor station at Maple, Ontario. A small increase in $CH_4$ was observed when the mobile lab was down wind of the compressor station as indicated on Figure 14.

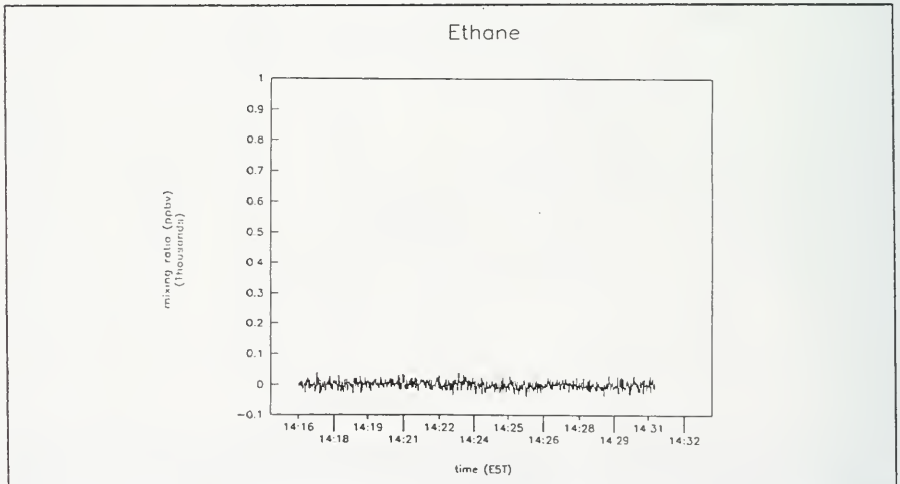



**Figure 16.** Measurements of $C_2H_6$ obtained during the third run following the route depicted in Figure 14 which encompassed the TCPL compressor station at Maple, Ontario. There is no evidence for $C_2H_6$ emissions at any time during the run (run average = $0 \pm 9$ ppbv).

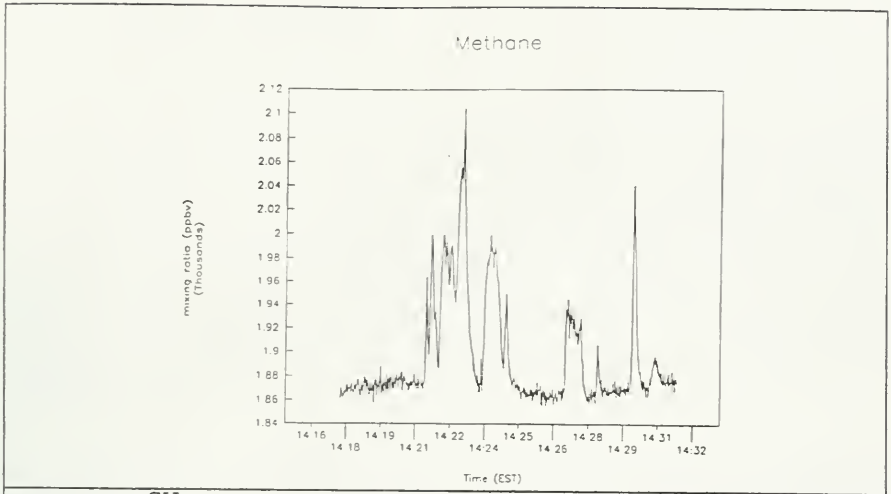



**Figure 17.** Detailed $CH_4$ measurements obtained during the third run while the mobile lab was stopped down wind of the TCPL compressor station at Maple, Ontario.

## 2.4 Summary First Years Effort

The EMS-50 system was configured to make simultaneous measurements of $CH_4$ and $C_2H_6$ with a time response sufficient to give good spatial resolution for measurements carried out from the Unisearch mobile laboratory moving at normal road speeds. Measurements were made at landfill, residential and industrial land use sites to provide a qualitative evaluation of the $CH_4$ emissions in these areas. The only major source of $CH_4$ measured was the Keele Valley Landfill. Measurements were also made along the natural gas distribution system and the only potential emission of natural gas was measured at the TCPL compressor station in Maple, Ontario but the levels were so low that confirmation of the source (natural gas or other $CH_4$ emitters) by the measurement of $C_2H_6$ was not possible as the $C_2H_6$ emissions were below the 10-20 ppbv detection limit of the instrumentation.

## 3.0 SECOND YEAR EFFORT

### 3.1 Measurement Program

The measurement program at the Keele Valley Landfill was conducted with the following objectives in mind. The data is to be used to understand and quantify the overall surface flux of the Keele Valley Landfill. The data would ultimately establish high points in the ambient $CH_4$ concentrations over the site and establish whether or not point source $CH_4$ emissions were present. The data can be used to estimate a potential reduction efficiency due to soil cover. The methodology for the measurement program is summarized below:

1) The Keele Valley Landfill was staked so as to divide the landfill into 38 sections, the dividing lines for the sections were based on the age of the landfill waste and its particular usage. Refer to Figure 18 for the location of the staked points at the Keele Valley Landfill.
2) Each section of the landfill was mapped for ambient $CH_4$ concentrations at two distinct heights above the surface. These being 10 cm and 1 meter. The $CH_4$ mapping of each section included both 10 second averages and a cumulative 5 minute average. The 10 second averages will yield maximum and minimum concentrations and the five minute averages will be used in the full scale landfill emission determination. Because of the difficulty in traversing the terrain at this Landfill a complete mapping of the landfill required two full measurement days. With aid in road clearing and the odd rescue by the Keele Valley staff we were able to make two complete mappings of the landfill. These problems could easily have been minimized had we installed the EMS-50 in an all terrain type vehicle. In situ calibrations were made after each sampling hour during ambient measurements and prior to each flux chamber measurement. All data was corrected for any variances in calibrations although the instrument never deviated more than 5% between subsequent calibrations.

3) Corresponding meteorological data was recorded for the sampling period, this included wind direction, wind speed and temperature.
4) To aid in modeling the landfill a total of 14 flux chamber measurements according to the EPA protocol were made. These were done on selected sections that best represented the whole scope of the landfill and included measurements of high, low and moderate emissions. The flux chamber method requires a one square meter chamber lined with Teflon to be placed over a selected location. The chamber is inserted in the ground so as to minimize leaks. Zero grade air is flowed into the chamber at a known rate, the trace gas concentrations will be monitored continuously by the EMS-50 while the zero air provides the background signal for the instrument. This would be the first flux chamber measurements of $CH_4$ using such a specific detector as the EMS-50. Derivation of the $CH_4$ flux can be made from these measurements
5) A total of three perimeter runs were made around the landfill to aid in the analysis of the flux calculation downwind of the boundary of the landfill site. Geopositional data was taken by way of an onboard GPS system. The sampling interval was reduced from 10 seconds to 2 seconds so as to aid in plume detection.
6) To see how the dispersion of $CH_4$ from the landfill affects areas downwind a full scale perimeter run at distances a few kilometers around the landfill was made.

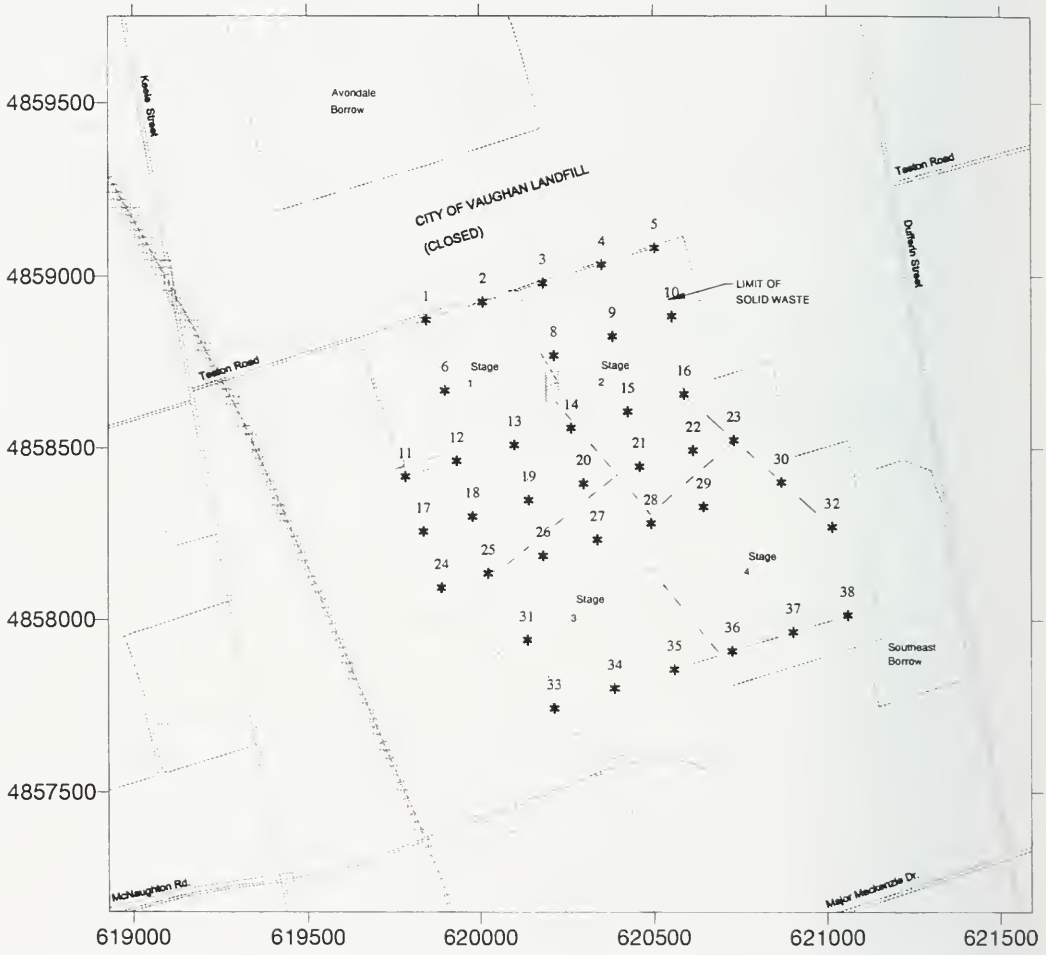
The measurement program at the Maple Natural Gas Distribution Centre consisted of a total of three perimeter runs around the station to deduce a first order approximation of $CH_4$ emissions. For these runs the EMS-50 was configured to do dual species monitoring to investigate the $CH_4/C_2H_6$ ratio. The sampling interval was set to one second. To see how the dispersion of $CH_4$ from this source affected areas downwind, at least two full scale perimeter runs at distance of one to five kilometers from the source were made.

### 3.2 Data Retrieval and Tabulation

Refer to Appendix A which shows the direct and continuous average for each sampling location over the 5 minute interval. Each sampling point is labeled in the bottom right hand corner. The height levels are designated by "L" which is the low height (10 cm) and "H" which is the high height (1 m). The final interval average is indicated above the last point. This is included to show the variability at each sampling location and the reason we took 5 minute averages. The $CH_4$ data was grouped into both 10 second and five minute averages for each subsection of each landfill at each height measured. The maximum, minimum and interval averages were tabulated with the corresponding meteorological data. The flux chamber emissions were determined and tabulated with corresponding ambient measurements. The perimeter run data was tabulated with the corresponding geopositional data. The data set was used in generating the models for the Keele Valley Landfill and used in a qualitative estimate for the emissions from the Maple Natural Gas Distribution Centre. The data analysis section was based on these two data sets.

## Figure 18

## Measurement Point Locations




* Measurement Point Location

## 3.3 Data Analysis

The data analysis was subdivided into two major sections, these being the surface flux measurements conducted with the flux chamber method and the ambient $CH_4$ measurements at the two heights above the surface. Plots of all ambient measurements at the Keele Valley Landfill depicting both 10 second and 5 minute cumulative averages can be found in Appendix A, at the end of this report. The modeled results and contour maps were prepared for Unisearch by SENES Consultants Limited. The surface plot of $CH_4$ over the landfill for October 6th was made utilizing both five minute and 2 minute averages.

### *3.3.1 Total Landfill Surface Flux Determination*

The $CH_4$ surface flux data utilizing the flux chamber methodology can be found on Table 1. The emission rates have been corrected for temperature gradients inside and outside of the flux chamber. The $CH_4$ data is presented as contours of constant flux overlaid on the Keele Valley Landfill site map. The measurement points are indicated as stars on the figure. Note that no measurements were taken in stages 3 and 4 because these areas have not been filled. By looking at the data there seems to be higher $CH_4$ flux through the surface on the east side of the landfill. This could be a result of what type of refuse was deposited at that location or possibly an indication of some problem with the gas collection system. From the flux data obtained it was possible to determine the total flux from the landfill. Zones of average flux were defined based on the data at each measurement location. The average flux in each zone was then multiplied by the zone areas to obtain an emission rate in grams/seconds. The total landfill emission rate of 1.4g/s was obtained by summing the emission rates over all the zones. The uncertainty in this value can be up to a factor of two due to the averaging over a zone.

## Table 1

## Surface Flux Measurements October - November 1994

| FLUX CHAMBER NUMBER | SAMPLING DATE | SAMPLING LOCATION | CORRECTED EMISSION RATE (ug/min/m²) | MEASURED AMBIENT CONCENTRATION (5 sec. average) (Contribution from all sources) (ppbv) | MODELLED AMBIENT CONCENTRATION (5 sec. average) (Contribution from landfill surface) (ppbv) |
|---|---|---|---|---|---|
| 1 | 31-Oct | POINT 18 | 13.36 | 10840 | 2027 |
| 2 | 31-Oct | POINT 20 | 222.70 | 26900 | 2231 |
| 3 | 31-Oct | POINT 22 | 503.63 | 53600 | 2213 |
| 4 | 31-Oct | POINT 12 | 16.42 | 17400 | 2105 |
| 5 | 31-Oct | POINT 24 | 1.68 | 2100 | 2079 |
| 6 | 02-Nov | POINT 26 | 104.50 | 10600 | 2051 |
| 7 | 02-Nov | POINT 28 | 35.27 | 6500 | 2078 |
| 8 | 02-Nov | POINT 14 | 62.48 | 16200 | 2032 |
| 9 | 02-Nov | POINT 16 | 10.36 | 10600 | 2007 |
| 10 | 11-Nov | POINT 30 | 5.76 | 5900 | 2004 |
| 11 | 11-Nov | POINT 06 | 1.12 | 2100 | 2000 |
| 12 | 11-Nov | POINT 08 | 55.00 | 8700 | 2016 |
| 13 | 11-Nov | POINT 10 | 3.34 | 2300 | 2005 |
| 14 | 11-Nov | POINT 36 | 1.88 | 1800 | 2103 |

Note: Background concentration 1820 ppb

### *3.3.2 Soil Cover Reduction Efficiency*

The U.S. EPA has developed the Landfill Gas Emissions Estimation Model (U.S. EPA 1991) to determine the production rate of gases over the age of a landfill. This is a first-order decay model based on the Scholl Canyon model. The model requires site-specific information regarding the amount of solid waste deposited at the Keele Valley Landfill. The U.S. EPA landfill model yields a total $CH_4$ flux of 4,606 $ft^3$/min. The landfill model adapted by Conestoga Rovers (SENES 1993) for the Keele Valley Landfill gives a range of total methane production of 5,000 to 8,500 $ft^3$/min. The U.S. EPA prediction is therefore equivalent to the lower bound of the range. However the Keele Valley Landfill has a gas collection system which was reported to have collected 4,100 $ft^3$/min during the time of the measurement program. Therefore the total amount of $CH_4$ released from the landfill is estimated to be 506 to 4,400 $ft^3$/min or 159 to 1,380 g/s. If the landfill only emits 1.4 g/s as indicated by the measured data we must surmise that the soil cover is 99% efficient at reducing $CH_4$ emissions. Even if the total flux were ten times higher than estimated (14 g/s) the soil cover would still be over 91% efficient.

### *3.3.3 Dispersion Model Simulation*

TRC Environmental Consultants has developed, in co-operation with the U.S. EPA, a model which accurately accounts for the behaviour of ground based sources of fugitive dust (TRC 1990) and has a good representation of area sources. The Fugitive Dust Model (FDM) is designed specifically to compute downwind concentrations and deposition rates of airborne particulate matter, using Gaussian dispersion and the incorporation of a gradient-transfer deposition algorithm to account for particulate deposition and plume depletion. However, FDM is also an excellent model to predict gaseous concentrations due to area sources.

The FDM has been accepted by the MOEE for landfill gaseous impact assessments (MOEE 1992). The modelers (SENES) have decided that the FDM is the most suitable model to study the Keele Valley Landfill.

The FDM requires the following inputs:

1) Estimated methane emissions;
2) Source geometry;
3) Receptor Locations;
4) Meteorology

Hourly meteorological inputs required by the FDM, are:

1) Wind direction and speed;
2) Stability class;
3) Ambient temperature;
4) Mixing height.

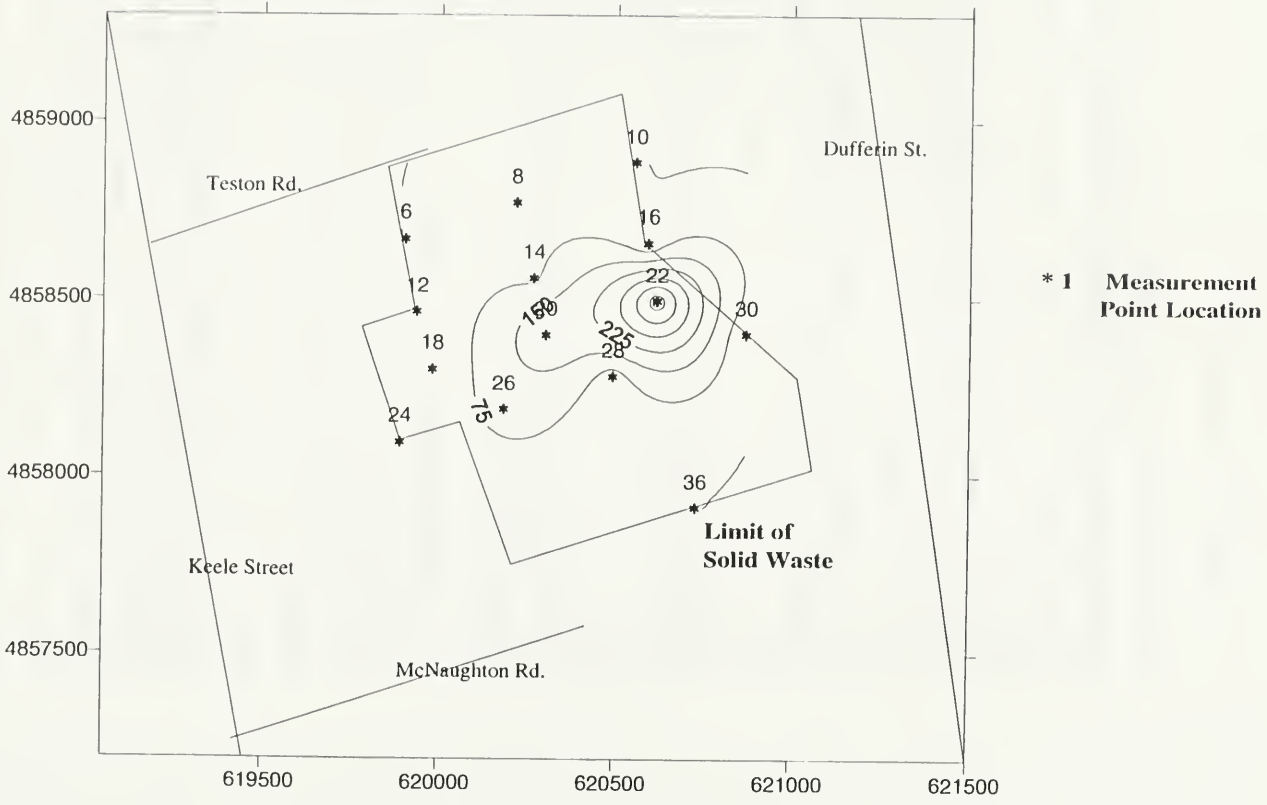
The surface flux data were used to derive emission rates of methane from different zones at the Keele Valley Landfill for input in the U.S. EPA Fugitive dust Model. This model was then utilized to calculate ambient methane concentrations at the locations of the surface flux measurements. The results are presented in Table 1. For comparison with ambient measurements taken at the same locations, the model predicted one-hour concentrations are converted to five-second averages using the equation

$$C_{5\,sec} = C_{1\,Hour} \times \left((3600\ sec)/(5\ sec)\right)^{0.2}$$

This equation assumes D stability. A background methane concentration of 1,820 ppbV, obtained from the data was added to the model predicted concentrations. The results indicate that the model predicted values are considerably lower than the measured data. Assuming the surface flux measurements are representative of the landfill, the model prediction indicates the contribution of only the estimated surface flux. The difference results from the contribution of other sources such as cracks in the cover, below surface leaks and other point sources.

# Figure 19

## Measured Methane Emission Rate (ug/m$^2$/min)



### *3.3.4 Ambient $CH_4$ Measurements*

The results of the ambient $CH_4$ mixing ratio measurements obtained with the TDLAS are presented as contour diagrams in Figures 20 to 27. Each figure represents the results for a single day at one height (either 10 cm or 1 meter) above the surface. The average measurements at each data point are given in Tables 2-1 to 2-8. The four days of ambient measurements on the landfill itself yields two complete mappings of the landfill. The measurements indicate that the maximum $CH_4$ concentrations occur in proximity to two locations, these being near S-17, S-25 and near S-20,S-21. It is also important to note that the highest surface flux measurement was made in the vicinity of S-21 at S-22. At locations where very large concentration gradients occur, for example point S-25 on October 6, 1994 where the 10 cm above surface measurement was 15.487 ppmV and the 1 meter above surface measurement was 5.067 ppmV it is likely that there is a point emission source located nearby. This point source is probably a leaking pipe or an open vent. This is indicated by the rapid diffusion in a relatively short distance (<1 m). At locations where the concentration gradient is not so large (points S-22 and S-23 taken that same sampling day), an area source such as a large crack in the cover may be contributing to the overall emissions.

### *3.3.5 Vertical Gradient in $CH_4$ Mixing Ratios*

A comparison between the mixing ratios at 1 meter above the surface (Figures 20, 22, 24 and 26) and at 10 cm above the surface (Figures 21, 23, 25 and 27) indicates that $CH_4$ concentrations are higher nearer to the surface. This trend is highly evident at locations near the maximum $CH_4$ values. As the lateral distance from these locations of high $CH_4$ values is increased the gradient decreases. This behaviour is consistent with the vertical profile of the horizontal wind component which increases with height above the ground and molecular diffusion principles. It is also important to note here that the higher the horizontal wind speed, the larger the vertical $CH_4$ concentration gradient. In a more general sense the effect of the horizontal wind component can be seen by the shape of the contours in Figures 20 to 27 and the prevailing wind direction indicated on the figures.

**Table 2-1**

**KEELE VALLEY LANDFILL $CH_4$ STUDY (1994) - AMBIENT MEASUREMENTS**

| DATE | 1 m above surface | | | | Meteorology | | |
|---|---|---|---|---|---|---|---|
| | SAMPLE POINT | SAMPLE START TIME | SAMPLE FINISH TIME | $CH_4$ POINT AVERAGE (ppbV) | Wind Speed (m/s) | Wind Direction (°) | Stability Class |
| 06-Oct | 1 | 14:36:00 | 14:41:00 | 3101 | 3.4 | 248 | 3 |
| 06-Oct | 2 | 14:49:00 | 14:54:00 | 2441 | 3.4 | 248 | 3 |
| 06-Oct | 3 | 15:04:00 | 15:09:00 | 3734 | 3.4 | 248 | 3 |
| 06-Oct | 4 | 15:18:00 | 15:23:00 | 3474 | 3.4 | 248 | 3 |
| 06-Oct | 5 | 15:39:00 | 15:44:00 | 5029 | 3 | 251 | 3 |
| 06-Oct | 6 | 14:23:00 | 14:28:00 | 1927 | 3.4 | 248 | 3 |
| 06-Oct | 10 | 15:53:00 | 15:58:00 | 4009 | 3 | 251 | 3 |
| 06-Oct | 11 | 13:15:00 | 13:20:00 | 1879 | 3.7 | 272 | 3 |
| 06-Oct | 12 | 14:04:00 | 14:09:00 | 1871 | 3.3 | 250 | 3 |
| 06-Oct | 16 | 16:07:00 | 16:12:00 | 4404 | 3 | 251 | 3 |
| 06-Oct | 17 | 13:31:00 | 13:36:00 | 1881 | 3.3 | 250 | 3 |
| 06-Oct | 22 | 16:22:00 | 16:27:00 | 4635 | 3 | 251 | 3 |
| 06-Oct | 23 | 16:37:00 | 16:42:00 | 6094 | 2.8 | 248 | 4 |
| 06-Oct | 24 | 13:46:00 | 13:51:00 | 1844 | 3.3 | 250 | 3 |
| 06-Oct | 25 | 12:55:00 | 13:00:00 | 5067 | 3.7 | 272 | 3 |
| 06-Oct | 31 | 12:37:00 | 12:42:00 | 1943 | 3.7 | 272 | 3 |
| 06-Oct | 33 | 12:21:00 | 12:26:00 | 1908 | 3.6 | 276 | 3 |
| 06-Oct | 34 | 12:05:00 | 12:10:00 | 1778 | 3.6 | 276 | 3 |
| 06-Oct | 35 | 11:48:00 | 11:53:00 | 1836 | 3.6 | 276 | 3 |
| 06-Oct | 36 | 16:55:00 | 17:00:00 | 3001 | 2.8 | 248 | 4 |

Table 2-2

KEELE VALLEY LANDFILL $CH_4$ STUDY (1994) - AMBIENT MEASUREMENTS

| DATE | 10 cm above surface | | | | Meteorology | | |
|---|---|---|---|---|---|---|---|
| | SAMPLE POINT | SAMPLE START TIME | SAMPLE FINISH TIME | $CH_4$ POINT AVERAGE (ppbV) | Wind Speed (m/s) | Wind Direction (°) | Stability Class |
| 06-Oct | 1 | 14:30:00 | 14:35:00 | 2485 | 3.4 | 248 | 3 |
| 06-Oct | 2 | 14:42:00 | 14:47:00 | 2948 | 3.4 | 248 | 3 |
| 06-Oct | 3 | 14:58:00 | 15:03:00 | 2413 | 3.4 | 248 | 3 |
| 06-Oct | 4 | 15:12:00 | 15:17:00 | 3352 | 3.4 | 248 | 3 |
| 06-Oct | 5 | 15:33:00 | 15:38:00 | 3941 | 3.0 | 251 | 3 |
| 06-Oct | 6 | 14:17:00 | 14:22:00 | 1907 | 3.3 | 250 | 3 |
| 06-Oct | 10 | 15:47:00 | 15:52:00 | 3289 | 3.0 | 251 | 3 |
| 06-Oct | 11 | 13:09:00 | 13:14:00 | 1829 | 3.7 | 272 | 3 |
| 06-Oct | 12 | 13:58:00 | 14:03:00 | 1867 | 3.3 | 250 | 3 |
| 06-Oct | 16 | 16:01:00 | 16:06:00 | 4661 | 3.0 | 251 | 3 |
| 06-Oct | 17 | 13:25:00 | 13:30:00 | 1921 | 3.7 | 272 | 3 |
| 06-Oct | 22 | 16:16:00 | 16:21:00 | 3649 | 3.0 | 251 | 3 |
| 06-Oct | 23 | 16:30:00 | 16:35:00 | 7684 | 2.8 | 248 | 4 |
| 06-Oct | 24 | 13:40:00 | 13:45:00 | 1904 | 3.3 | 250 | 3 |
| 06-Oct | 25 | 12:48:00 | 12:53:00 | 15487 | 3.7 | 272 | 3 |
| 06-Oct | 31 | 12:31:00 | 12:36:00 | 1865 | 3.7 | 272 | 3 |
| 06-Oct | 33 | 12:15:00 | 12:20:00 | 1865 | 3.6 | 276 | 3 |
| 06-Oct | 34 | 11:58:00 | 12:03:00 | 1793 | 3.6 | 276 | 3 |
| 06-Oct | 35 | 11:42:00 | 11:47:00 | 1901 | 3.6 | 276 | 3 |
| 06-Oct | 36 | 16:49:00 | 16:54:00 | 7967 | 2.8 | 248 | 4 |

Table 2-3

## KEELE VALLEY LANDFILL $CH_4$ STUDY (1994) - AMBIENT MEASUREMENTS

| DATE | 1 m above surface | | | | Meteorology | | |
|---|---|---|---|---|---|---|---|
| | SAMPLE POINT | SAMPLE START TIME | SAMPLE FINISH TIME | $CH_4$ POINT AVERAGE (ppbV) | Wind Speed (m/s) | Wind Direction (°) | Stability Class |
| 07-Oct | 8 | 13:55:00 | 14:00:00 | 12119 | 3.4 | 196 | 3 |
| 07-Oct | 9 | 13:26:00 | 13:31:00 | 3662 | 3.6 | 216 | 3 |
| 07-Oct | 14 | 12:57:00 | 13:02:00 | 3828 | 3.6 | 216 | 3 |
| 07-Oct | 15 | 13:11:00 | 13:16:00 | 3410 | 3.6 | 216 | 3 |
| 07-Oct | 18 | 11:49:00 | 11:54:00 | 8235 | 4.1 | 230 | 4 |
| 07-Oct | 19 | 12:05:00 | 12:10:00 | 7478 | 4.1 | 230 | 4 |
| 07-Oct | 20 | 12:20:00 | 12:25:00 | 16499 | 4.1 | 230 | 4 |
| 07-Oct | 21 | 12:40:00 | 12:45:00 | 4681 | 3.6 | 216 | 3 |
| 07-Oct | 26 | 14:47:00 | 14:52:00 | 9733 | 4.7 | 202 | 4 |
| 07-Oct | 27 | 14:59:00 | 15:04:00 | 9499 | 4.7 | 202 | 4 |
| 07-Oct | 28 | 15:11:00 | 15:16:00 | 15255 | 4.7 | 202 | 4 |
| 07-Oct | 29 | 15:23:00 | 15:28:00 | 9909 | 4.7 | 202 | 4 |
| 07-Oct | 30 | 15:36:00 | 15:41:00 | 10187 | 4.6 | 197 | 4 |
| 07-Oct | 32 | 15:49:00 | 15:54:00 | 2137 | 4.6 | 197 | 4 |
| 07-Oct | 37 | 16:15:00 | 16:20:00 | 2001 | 4.6 | 197 | 4 |
| 07-Oct | 38 | 16:02:00 | 16:07:00 | 2015 | 4.6 | 197 | 4 |

**Table 2-4**

**KEELE VALLEY LANDFILL $CH_4$ STUDY (1994) - AMBIENT MEASUREMENTS**

| DATE | 10 cm above surface | | | | Meteorology | | |
|---|---|---|---|---|---|---|---|
| | SAMPLE POINT | SAMPLE START TIME | SAMPLE FINISH TIME | $CH_4$ POINT AVERAGE (ppbV) | Wind Speed (m/s) | Wind Direction (°) | Stability Class |
| 07-Oct | 8 | 13:49:00 | 13:54:00 | 11553 | 3.4 | 196 | 3 |
| 07-Oct | 9 | 13:20:00 | 13:25:00 | 5470 | 3.6 | 216 | 3 |
| 07-Oct | 14 | 12:51:00 | 12:56:00 | 4378 | 3.6 | 216 | 3 |
| 07-Oct | 15 | 13:05:00 | 13:10:00 | 3713 | 3.6 | 216 | 3 |
| 07-Oct | 18 | 11:43:00 | 11:48:00 | 7710 | 4.1 | 230 | 4 |
| 07-Oct | 19 | 11:59:00 | 12:04:00 | 8448 | 4.1 | 230 | 4 |
| 07-Oct | 20 | 12:14:00 | 12:19:00 | 12829 | 4.1 | 230 | 4 |
| 07-Oct | 21 | 12:34:00 | 12:39:00 | 5634 | 3.6 | 216 | 3 |
| 07-Oct | 26 | 14:40:00 | 14:45:00 | 11047 | 4.7 | 202 | 4 |
| 07-Oct | 27 | 14:53:00 | 14:58:00 | 9723 | 4.7 | 202 | 4 |
| 07-Oct | 28 | 15:05:00 | 15:10:00 | 16337 | 4.7 | 202 | 4 |
| 07-Oct | 29 | 15:17:00 | 15:22:00 | 8418 | 4.7 | 202 | 4 |
| 07-Oct | 30 | 15:30:00 | 15:35:00 | 9978 | 4.6 | 197 | 4 |
| 07-Oct | 32 | 15:43:00 | 15:48:00 | 2331 | 4.6 | 197 | 4 |
| 07-Oct | 37 | 16:09:00 | 16:14:00 | 2000 | 4.6 | 197 | 4 |
| 07-Oct | 38 | 15:56:00 | 16:01:00 | 1991 | 4.6 | 197 | 4 |

Table 2-5

## KEELE VALLEY LANDFILL $CH_4$ STUDY (1994) - AMBIENT MEASUREMENTS

| DATE | 1 m above surface | | | | Meteorology | | |
|---|---|---|---|---|---|---|---|
| | SAMPLE POINT | SAMPLE START TIME | SAMPLE FINISH TIME | $CH_4$ POINT AVERAGE (ppbV) | Wind Speed (m/s) | Wind Direction (°) | Stability Class |
| 12-Oct | 1 | 13:51:00 | 13:56:00 | 4262 | 1.8 | 146 | 1 |
| 12-Oct | 2 | 14:03:00 | 14:08:00 | 6691 | 1.8 | 146 | 1 |
| 12-Oct | 3 | 14:15:00 | 14:20:00 | 3939 | 1.8 | 146 | 1 |
| 12-Oct | 4 | 14:28:00 | 14:33:00 | 3115 | 1.8 | 146 | 1 |
| 12-Oct | 5 | 14:42:00 | 14:47:00 | 1850 | 2.1 | 161 | 1 |
| 12-Oct | 6 | 13:39:00 | 13:44:00 | 4337 | 1.8 | 146 | 1 |
| 12-Oct | 10 | 14:56:00 | 15:01:00 | 1832 | 2.1 | 161 | 1 |
| 12-Oct | 11 | 12:46:00 | 12:51:00 | 9621 | 1.8 | 152 | 2 |
| 12-Oct | 12 | 13:27:00 | 13:32:00 | 7942 | 1.8 | 152 | 2 |
| 12-Oct | 16 | 15:08:00 | 15:13:00 | 2986 | 2.1 | 161 | 1 |
| 12-Oct | 17 | 12:59:00 | 13:04:00 | 10994 | 1.8 | 152 | 2 |
| 12-Oct | 22 | 15:21:00 | 15:26:00 | 2561 | 2.1 | 161 | 1 |
| 12-Oct | 23 | 15:33:00 | 15:38:00 | 1818 | 2.1 | 125 | 2 |
| 12-Oct | 24 | 13:11:00 | 13:16:00 | 2492 | 1.8 | 152 | 2 |
| 12-Oct | 25 | 12:32:00 | 12:37:00 | 2155 | 1.8 | 152 | 2 |
| 12-Oct | 30 | 15:46:00 | 15:51:00 | 1855 | 2.1 | 125 | 2 |
| 12-Oct | 31 | 12:16:00 | 12:21:00 | 2655 | 2.1 | 138 | 3 |
| 12-Oct | 32 | 15:59:00 | 16:04:00 | 1834 | 2.1 | 125 | 2 |
| 12-Oct | 33 | 12:03:00 | 12:08:00 | 2234 | 2.1 | 138 | 3 |
| 12-Oct | 34 | 11:51:00 | 11:56:00 | 1829 | 2.1 | 138 | 3 |
| 12-Oct | 35 | 11:33:00 | 11:38:00 | 2094 | 2.1 | 138 | 3 |
| 12-Oct | 36 | 16:39:00 | 16:44:00 | 1840 | 3.1 | 116 | 3 |
| 12-Oct | 37 | 16:23:00 | 16:28:00 | 1934 | 2.1 | 125 | 2 |
| 12-Oct | 38 | 16:11:00 | 16:16:00 | 1831 | 2.1 | 125 | 2 |

**Table 2-6**

**KEELE VALLEY LANDFILL $CH_4$ STUDY (1994) - AMBIENT MEASUREMENTS**

| DATE | 10 cm above surface | | | | Meteorology | | |
|---|---|---|---|---|---|---|---|
| | SAMPLE POINT | SAMPLE START TIME | SAMPLE FINISH TIME | $CH_4$ POINT AVERAGE (ppbV) | Wind Speed (m/s) | Wind Direction (°) | Stability Class |
| 12-Oct | 1 | 13:45:00 | 13:50:00 | 2979 | 1.8 | 146 | 1 |
| 12-Oct | 2 | 13:57:00 | 14:02:00 | 5650 | 1.8 | 146 | 1 |
| 12-Oct | 3 | 14:09:00 | 14:14:00 | 2596 | 1.8 | 146 | 1 |
| 12-Oct | 4 | 14:22:00 | 14:27:00 | 2081 | 1.8 | 146 | 1 |
| 12-Oct | 5 | 14:36:00 | 14:41:00 | 1837 | 2.1 | 161 | 1 |
| 12-Oct | 6 | 13:33:00 | 13:38:00 | 5050 | 1.8 | 146 | 1 |
| 12-Oct | 10 | 14:50:00 | 14:55:00 | 1877 | 2.1 | 161 | 1 |
| 12-Oct | 11 | 12:40:00 | 12:45:00 | 9082 | 1.8 | 152 | 2 |
| 12-Oct | 12 | 13:21:00 | 13:26:00 | 9726 | 1.8 | 152 | 2 |
| 12-Oct | 16 | 15:02:00 | 15:07:00 | 1994 | 2.1 | 161 | 1 |
| 12-Oct | 17 | 12:53:00 | 12:58:00 | 15636 | 1.8 | 152 | 2 |
| 12-Oct | 22 | 15:15:00 | 15:20:00 | 2787 | 2.1 | 161 | 1 |
| 12-Oct | 23 | 15:27:00 | 15:32:00 | 1847 | 2.1 | 161 | 1 |
| 12-Oct | 24 | 13:05:00 | 13:10:00 | 2868 | 1.8 | 152 | 2 |
| 12-Oct | 25 | 12:26:00 | 12:31:00 | 2128 | 2.1 | 138 | 3 |
| 12-Oct | 30 | 15:40:00 | 15:45:00 | 1823 | 2.1 | 125 | 2 |
| 12-Oct | 31 | 12:10:00 | 12:15:00 | 3505 | 2.1 | 138 | 3 |
| 12-Oct | 32 | 15:53:00 | 15:58:00 | 1849 | 2.1 | 125 | 2 |
| 12-Oct | 33 | 11:57:00 | 12:02:00 | 2288 | 2.1 | 138 | 3 |
| 12-Oct | 34 | 11:45:00 | 11:50:00 | 1921 | 2.1 | 138 | 3 |
| 12-Oct | 35 | 11:27:00 | 11:32:00 | 2067 | 3.1 | 114 | 4 |
| 12-Oct | 36 | 16:33:00 | 16:38:00 | 1846 | 3.1 | 116 | 3 |
| 12-Oct | 37 | 16:17:00 | 16:22:00 | 1871 | 2.1 | 125 | 2 |
| 12-Oct | 38 | 16:05:00 | 16:10:00 | 1838 | 2.1 | 125 | 2 |

**Table 2-7**

## KEELE VALLEY LANDFILL $CH_4$ STUDY (1994) - AMBIENT MEASUREMENTS

| DATE | 1 m above surface | | | | Meteorology | | |
|---|---|---|---|---|---|---|---|
| | SAMPLE POINT | SAMPLE START TIME | SAMPLE FINISH TIME | $CH_4$ POINT AVERAGE (ppbV) | Wind Speed (m/s) | Wind Direction (°) | Stability Class |
| 23-Oct | 13 | 15:23:00 | 15:28:00 | 10692 | 2.5 | 249 | 4 |
| 23-Oct | 14 | 15:10:00 | 15:15:00 | 9786 | 2.5 | 249 | 4 |
| 23-Oct | 15 | 15:35:00 | 15:40:00 | 11676 | 4.2 | 269 | 4 |
| 23-Oct | 18 | 14:21:00 | 14:26:00 | 18137 | 2.5 | 245 | 4 |
| 23-Oct | 19 | 14:33:00 | 14:38:00 | 11304 | 2.5 | 249 | 4 |
| 23-Oct | 20 | 14:45:00 | 14:50:00 | 23754 | 2.5 | 249 | 4 |
| 23-Oct | 21 | 14:58:00 | 15:03:00 | 18676 | 2.5 | 249 | 4 |
| 23-Oct | 26 | 13:59:00 | 14:04:00 | 10814 | 2.5 | 245 | 4 |
| 23-Oct | 26 | 12:51:00 | 12:56:00 | 7543 | 1.6 | 252 | 3 |
| 23-Oct | 27 | 13:03:00 | 13:08:00 | 14005 | 1.6 | 252 | 3 |
| 23-Oct | 28 | 13:16:00 | 13:21:00 | 14576 | 1.6 | 252 | 3 |
| 23-Oct | 29 | 13:31:00 | 13:36:00 | 9590 | 2.5 | 245 | 4 |
| 23-Oct | 30 | 13:45:00 | 13:50:00 | 9566 | 2.5 | 245 | 4 |
| 23-Oct | 35 | 12:34:00 | 12:39:00 | 6591 | 1.6 | 252 | 3 |

**Table 2-8**

**KEELE VALLEY LANDFILL $CH_4$ STUDY (1994) - AMBIENT MEASUREMENTS**

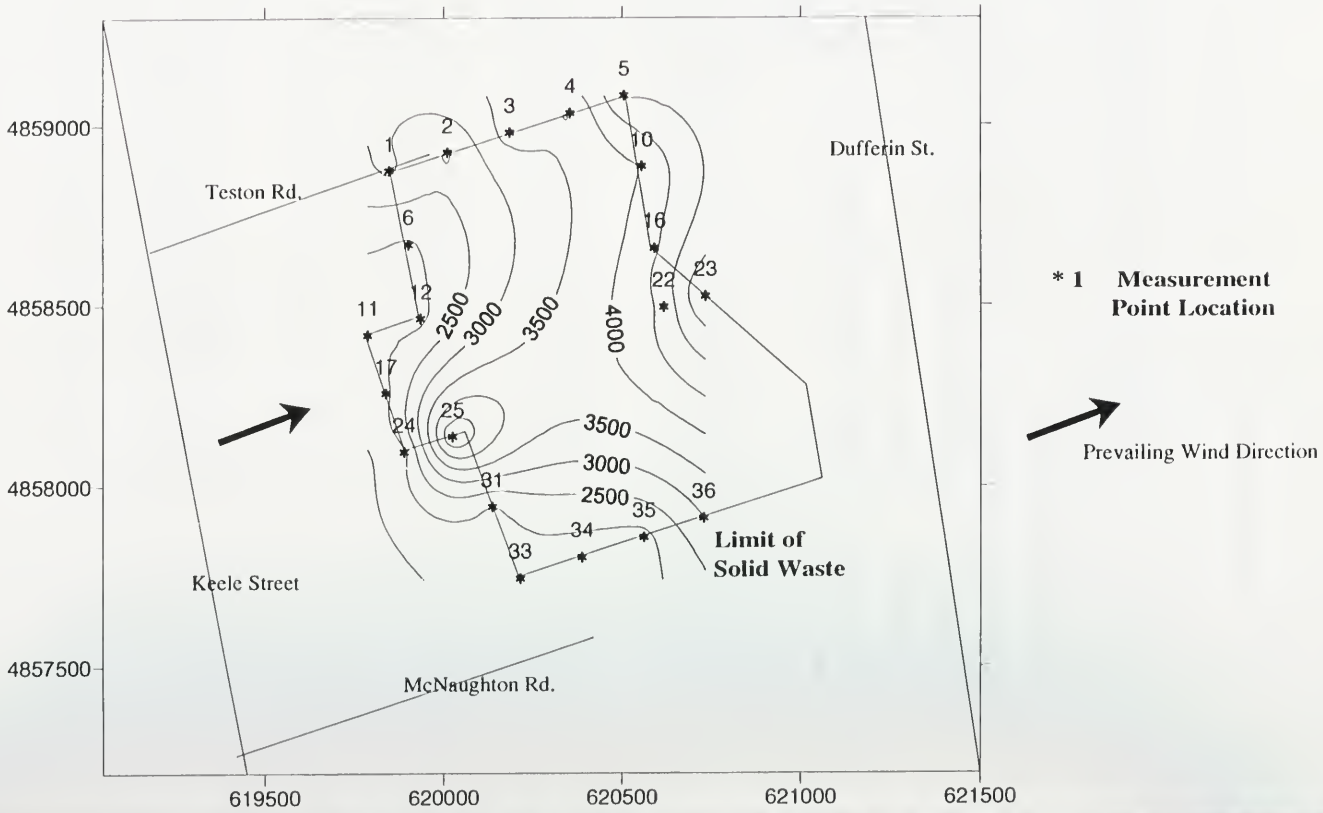
| DATE | 10 cm above surface | | | | Meteorology | | |
|---|---|---|---|---|---|---|---|
| | SAMPLE POINT | SAMPLE START TIME | SAMPLE FINISH TIME | $CH_4$ POINT AVERAGE (ppbV) | Wind Speed (m/s) | Wind Direction (°) | Stability Class |
| 23-Oct | 13 | 15:17:00 | 15:22:00 | 9364 | 2.5 | 249 | 4 |
| 23-Oct | 14 | 15:04:00 | 15:09:00 | 11828 | 2.5 | 249 | 4 |
| 23-Oct | 15 | 15:29:00 | 15:34:00 | 10393 | 4.2 | 269 | 4 |
| 23-Oct | 18 | 14:15:00 | 14:20:00 | 17434 | 2.5 | 245 | 4 |
| 23-Oct | 19 | 14:27:00 | 14:32:00 | 14795 | 2.5 | 249 | 4 |
| 23-Oct | 20 | 14:39:00 | 14:44:00 | 14206 | 2.5 | 249 | 4 |
| 23-Oct | 21 | 14:52:00 | 14:57:00 | 21391 | 2.5 | 249 | 4 |
| 23-Oct | 26 | 12:45:00 | 12:50:00 | 6912 | 1.6 | 252 | 3 |
| 23-Oct | 26 | 13:53:00 | 13:58:00 | 9321 | 2.5 | 245 | 4 |
| 23-Oct | 27 | 12:57:00 | 13:02:00 | 15692 | 1.6 | 252 | 3 |
| 23-Oct | 28 | 13:10:00 | 13:15:00 | 10240 | 1.6 | 252 | 3 |
| 23-Oct | 29 | 13:25:00 | 13:30:00 | 9269 | 1.6 | 252 | 3 |
| 23-Oct | 30 | 13:39:00 | 13:44:00 | 10457 | 2.5 | 245 | 4 |
| 23-Oct | 35 | 12:28:00 | 12:33:00 | 5848 | 1.5 | 219 | 2 |

### *3.3.6 Comparison of Methane Mixing Ratios Between Measured and Modeled Data*

The Fugitive Dust Model was employed to simulate the ambient mixing ratios measured (Figures 20 to 27). The $CH_4$ emission rates were determined using the surface flux measurements as the data base for the model. The results of the model calculations are presented in Figures 28 to 31 for comparison with Figures 20 to 27. The shapes of the contours are roughly the same. The model calculations yield smaller values then the measured data, with maximum deviation occurring at locations of highest ambient measurements. This indicates that surface flux measurements alone cannot explain the high concentrations measured and does not account for major contributions of methane emissions by other sources. These sources are likely to be from cracks in the covers, leaking pipes, pumps, valves or other point sources. The highest ambient methane mixing ratios on the west side of the site occur in the vicinity of S-25 and S-17. This location is where one of the main gas headers runs along perimeter of the site.

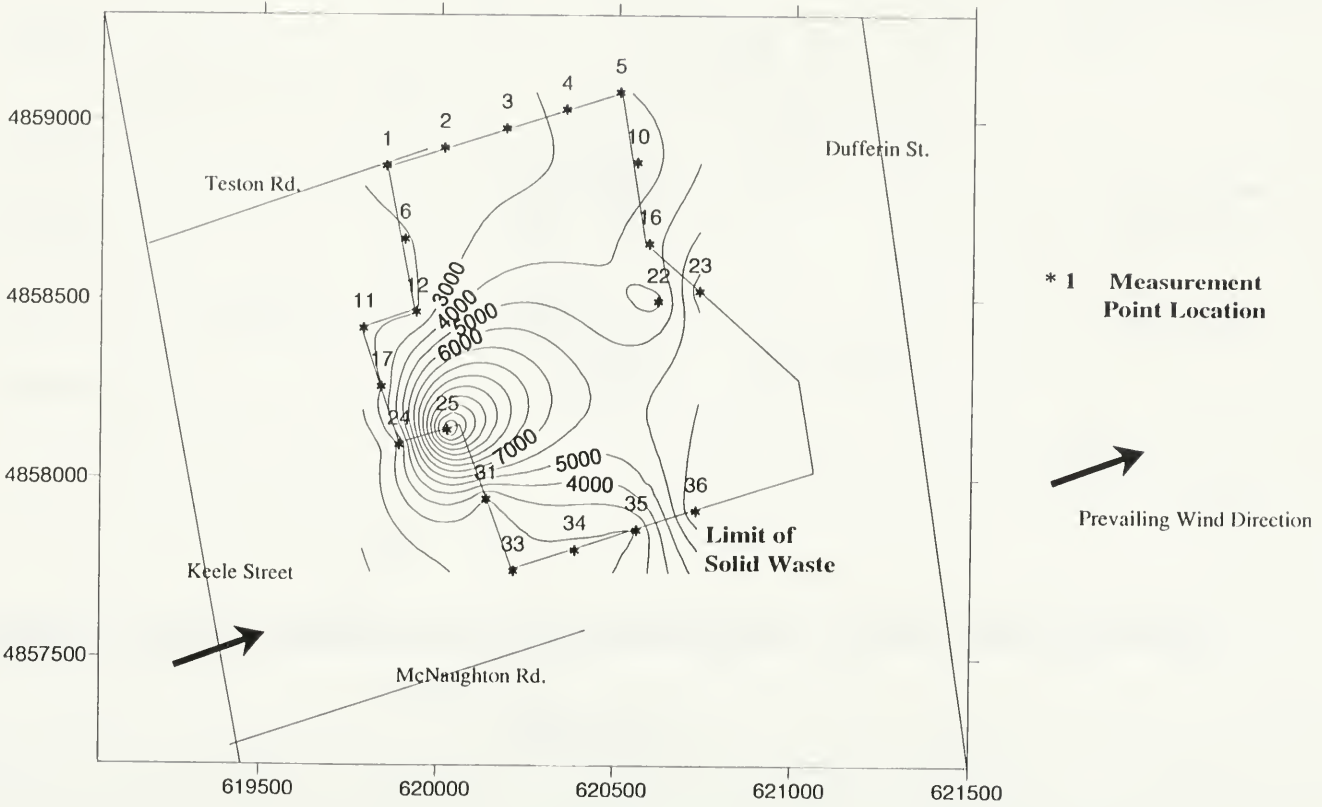
# Figure 20

## October 6, 1994 - Methane Concentrations (ppb) - 1 Metre Above Surface



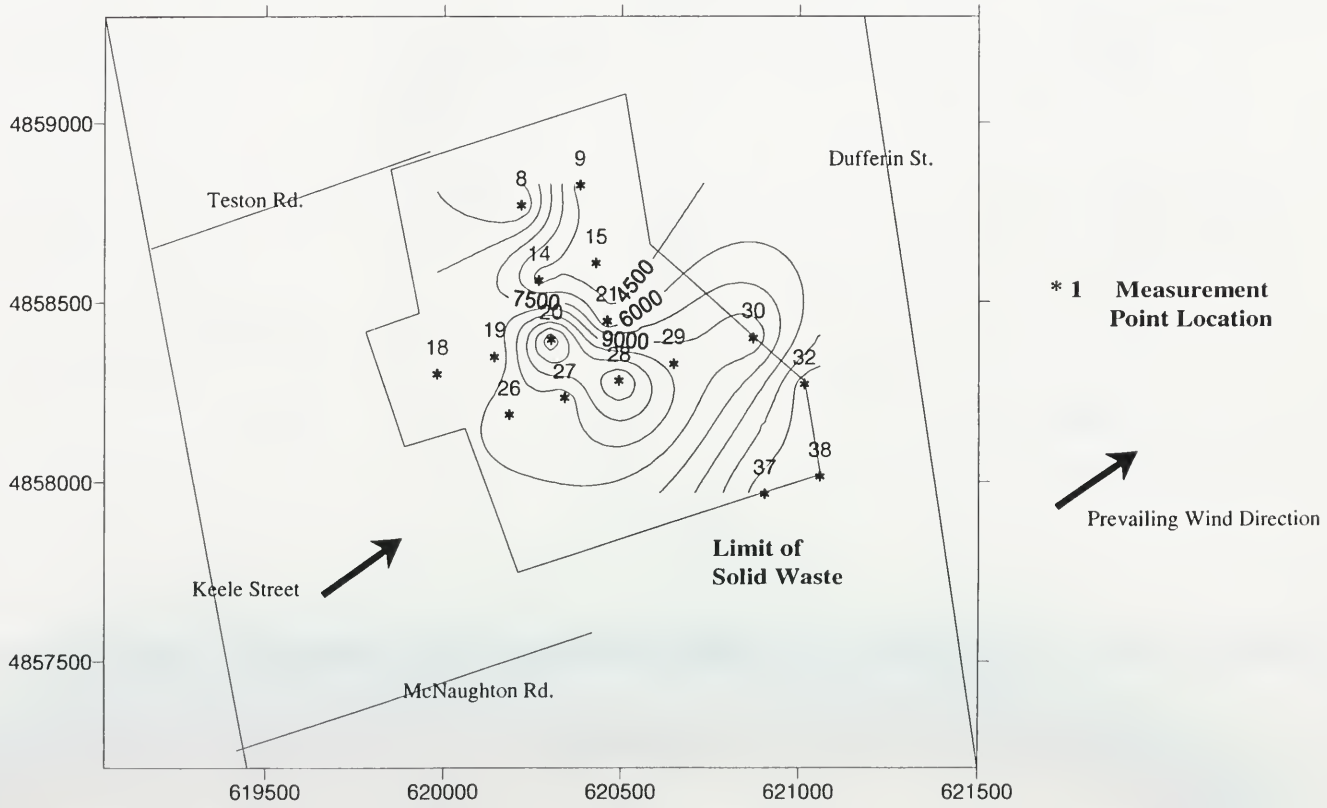
# Figure 21

## October 6, 1994 - Methane Concentrations (ppb) - 10 Centimetres Above Surface



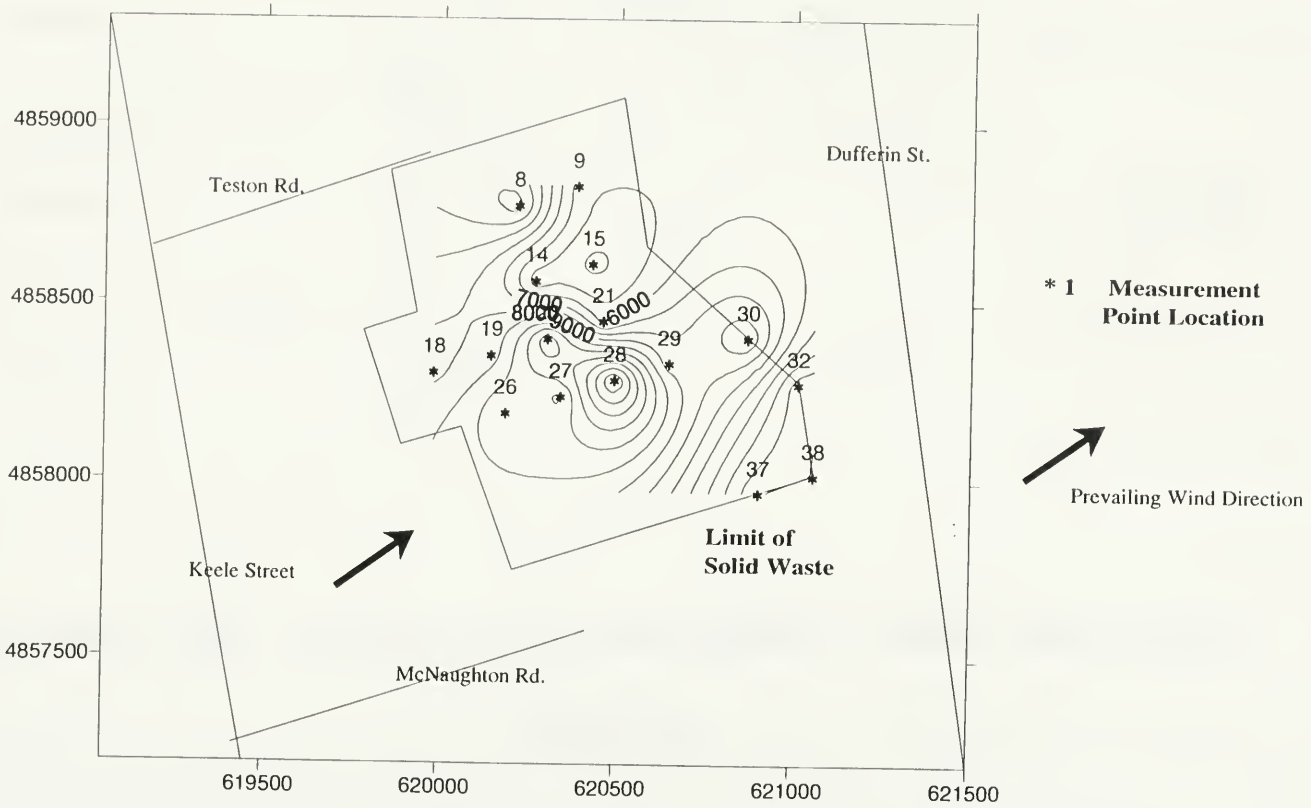
# Figure 22

## October 7, 1994 - Methane Concentrations (ppb) - 1 Metre Above Surface



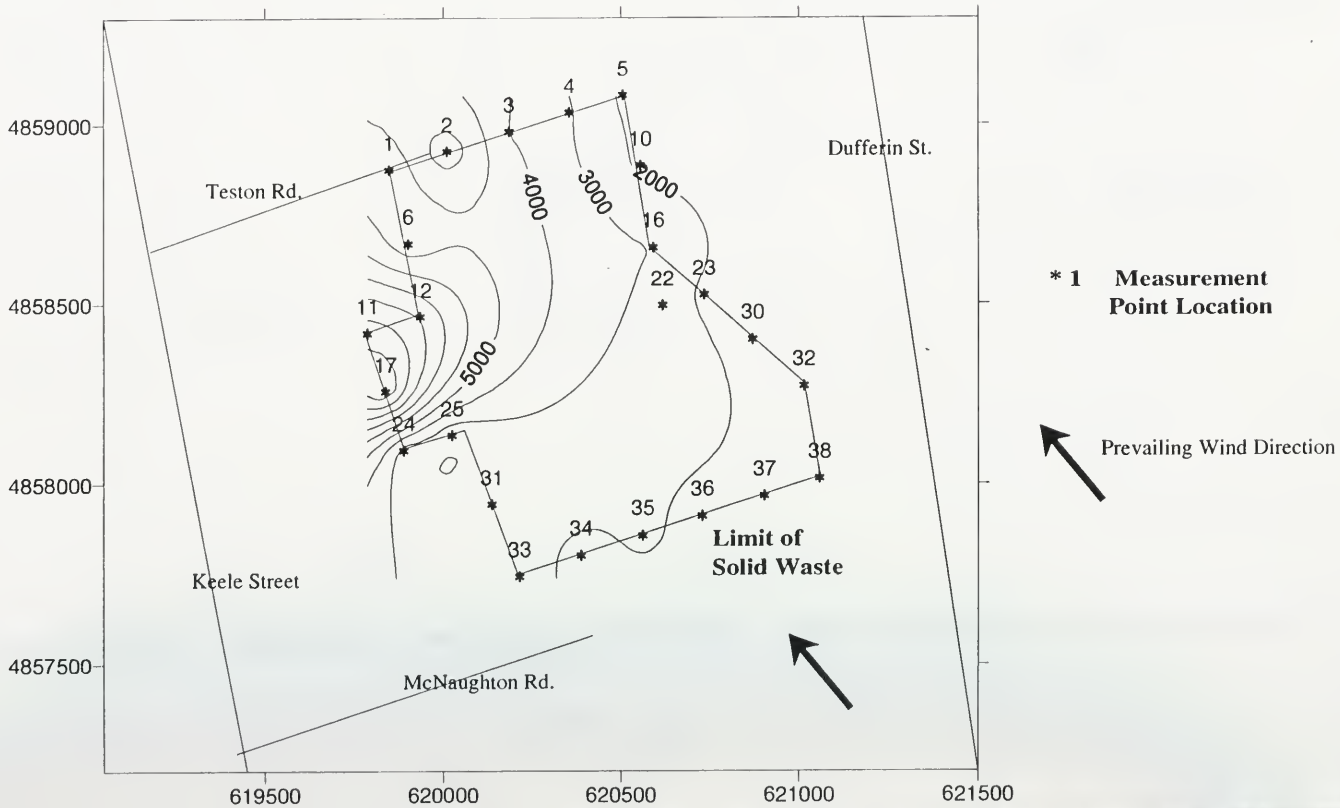
# Figure 23

## October 7, 1994 - Methane Concentrations (ppb) - 10 Centimetres Above Surface



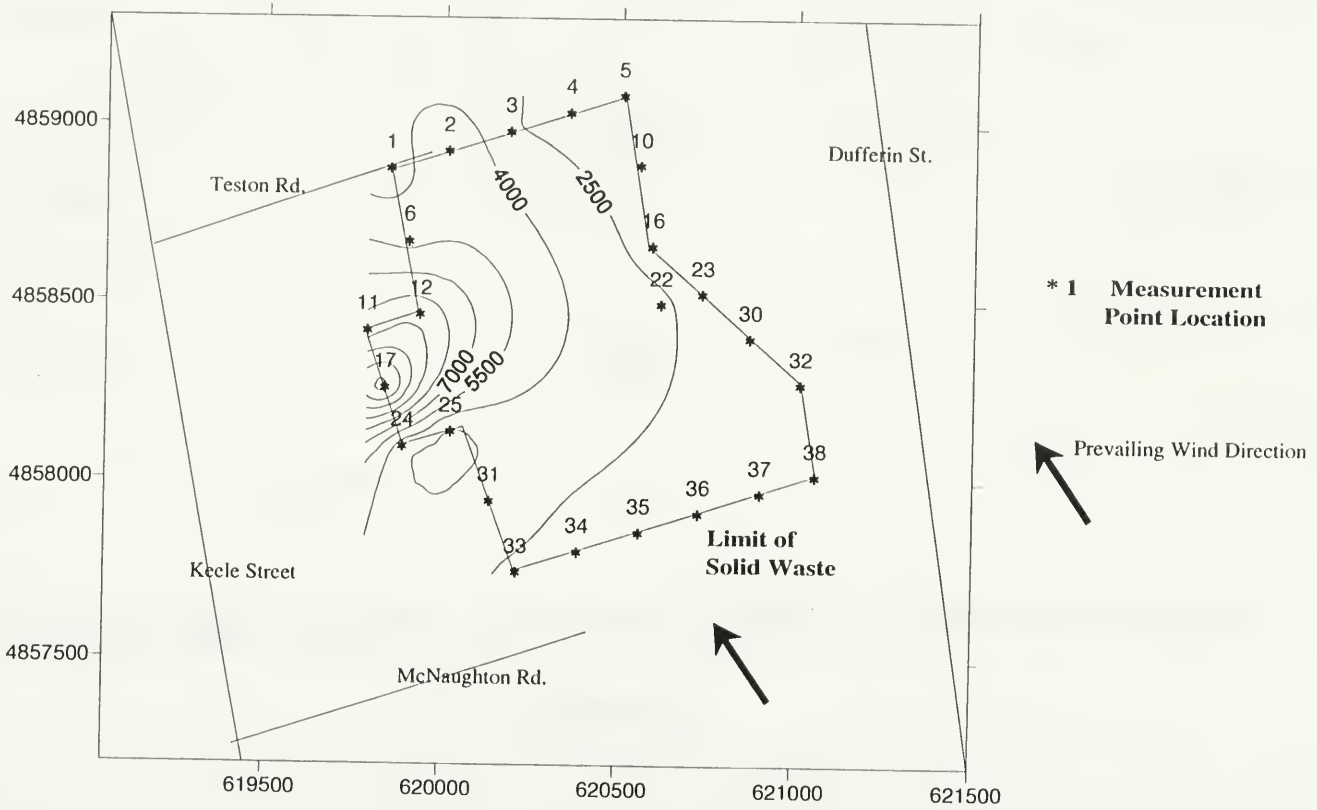
# Figure 24

## October 12, 1994 - Methane Concentrations (ppb) - 1 Metre Above Surface



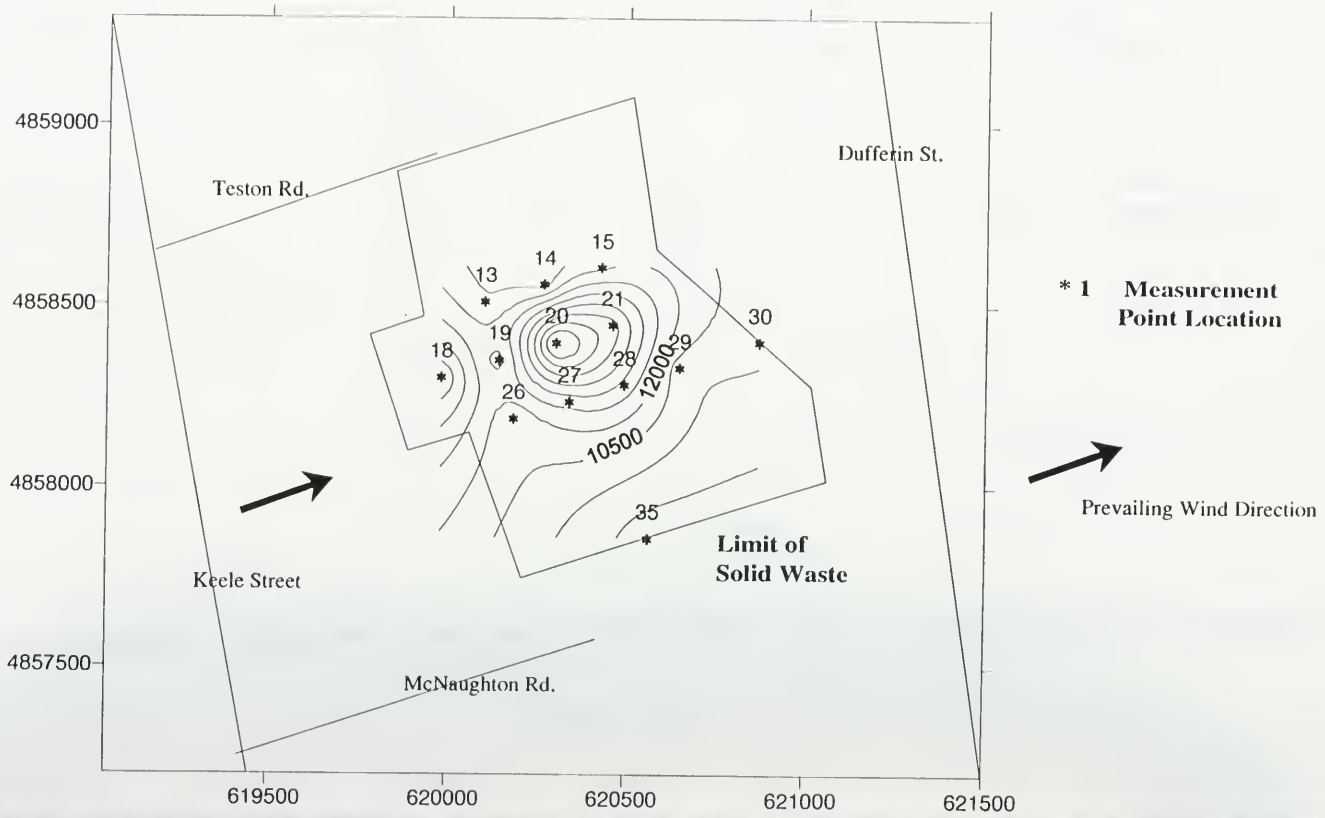
# Figure 25

## October 12, 1994 - Methane Concentrations (ppb) - 10 Centimetres Above Surface



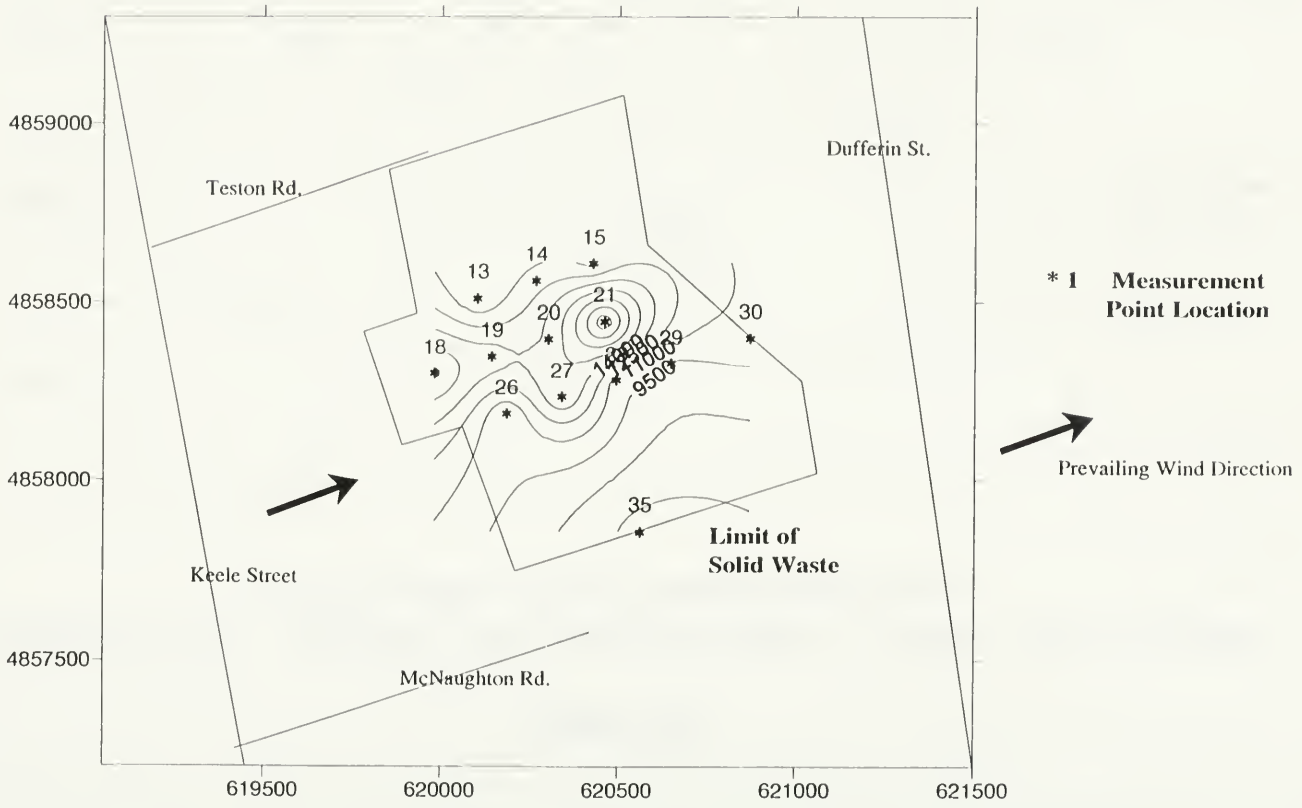
# Figure 26

## October 23, 1994 - Methane Concentrations (ppb) - 1 Metre Above Surface



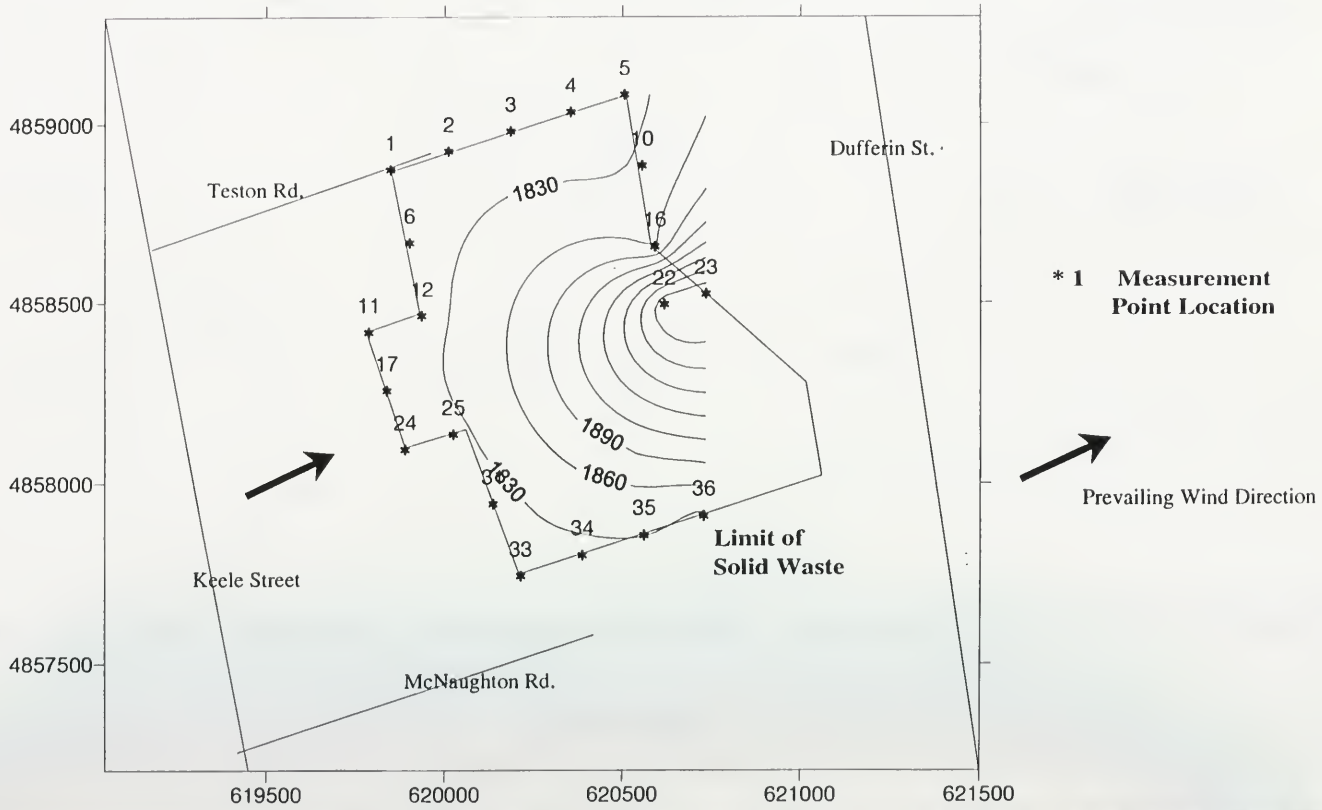
# Figure 27

## October 23, 1994 - Methane Concentrations (ppb) - 10 Centimetres Above Surface



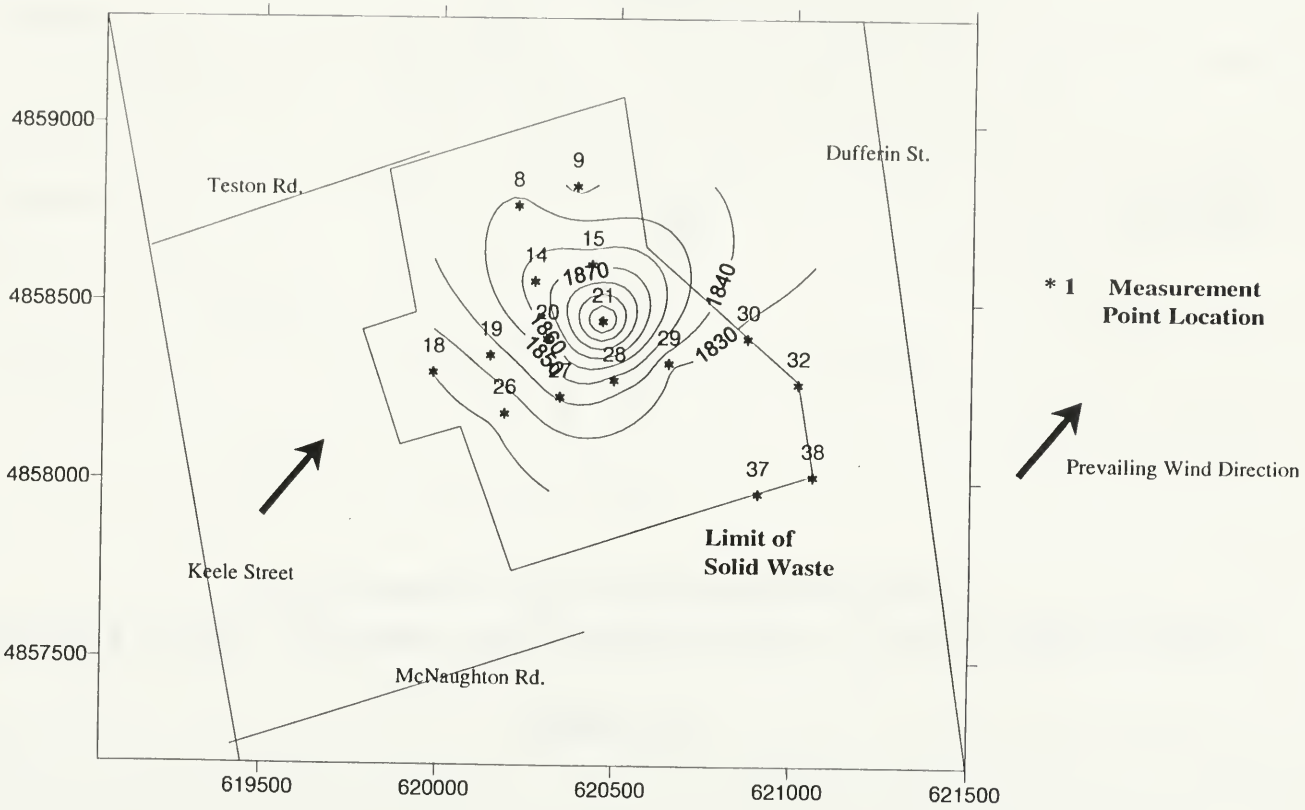
# Figure 28

## October 6, 1994 - Methane Concentrations (ppb) - 1 Metre Above Surface
## FDM Results - Flux Measurements Only



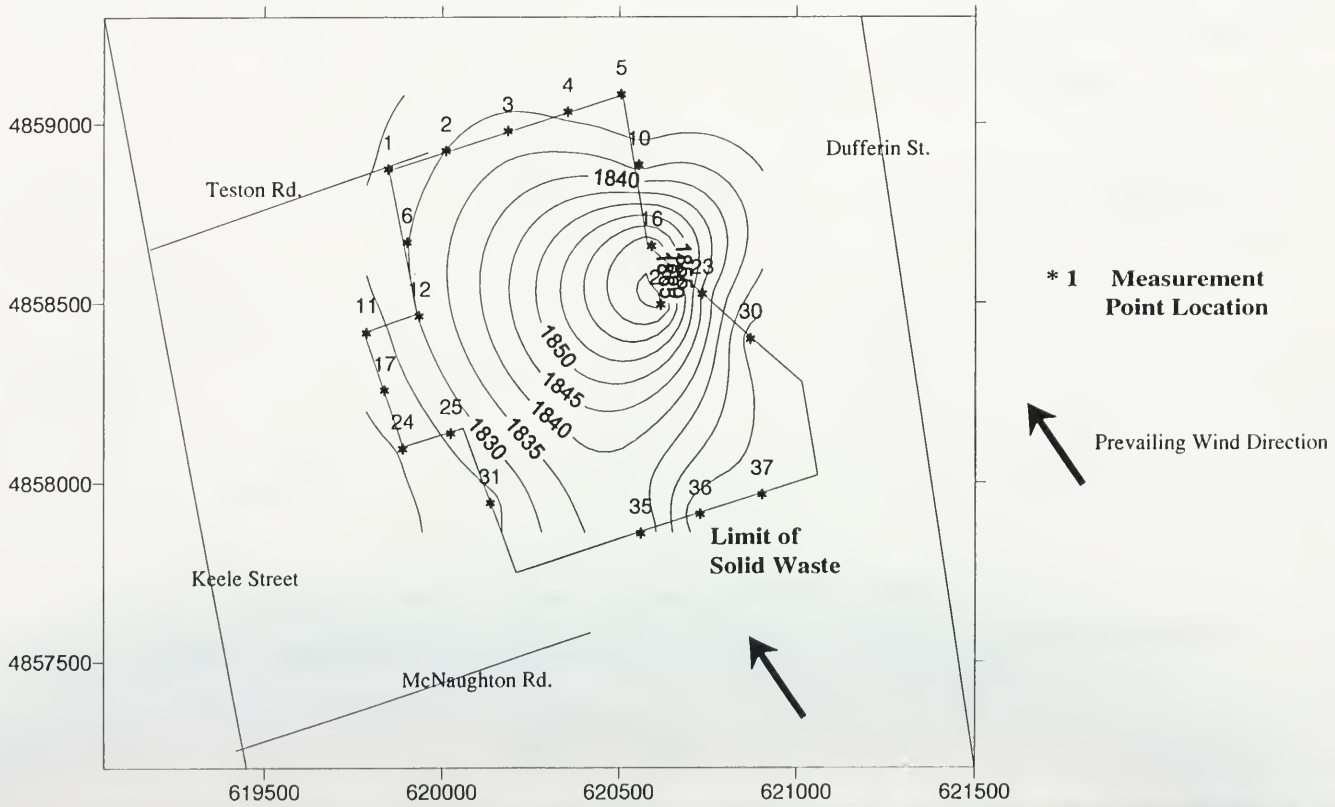
# Figure 29

## October 7, 1994 - Methane Concentrations (ppb) - 1 Metre Above Surface
## FDM Results - Flux Measurements Only



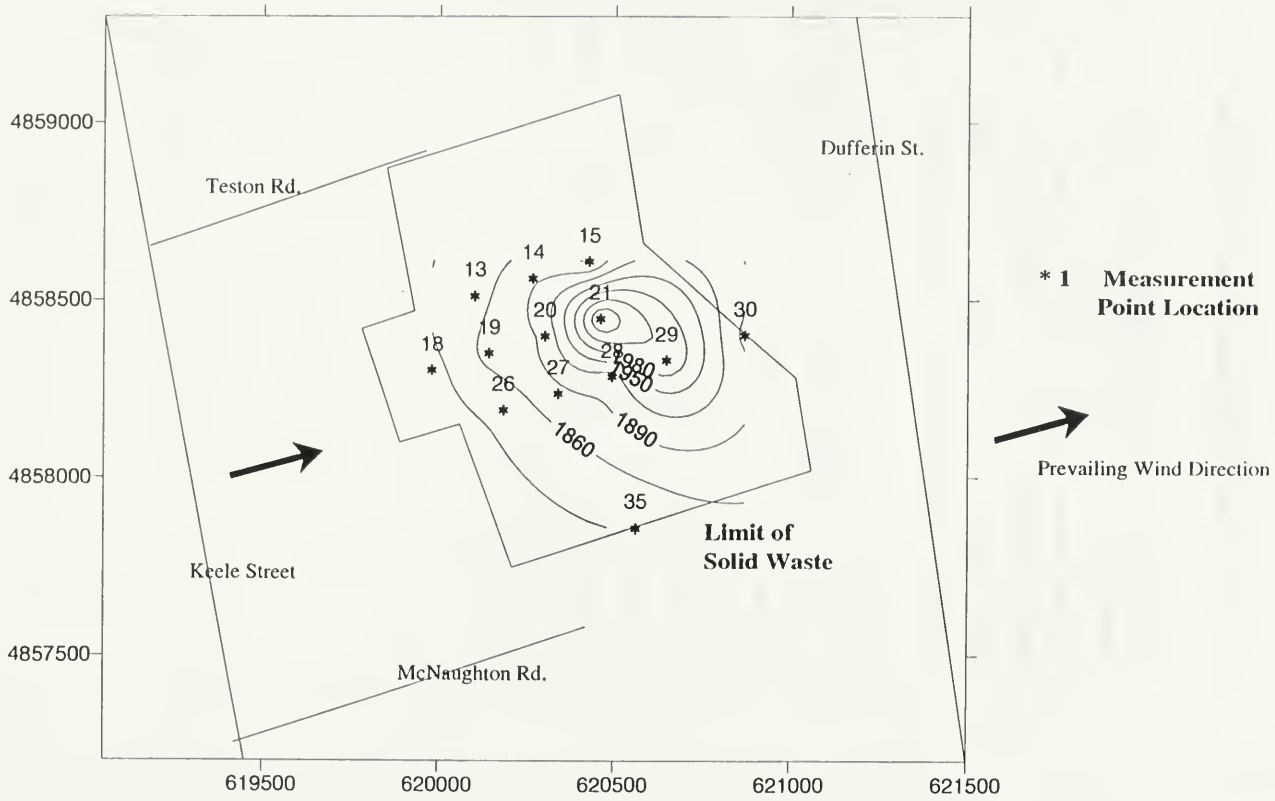
# Figure 30

## October 12, 1994 - Methane Concentrations (ppb) - 1 Metre Above Surface
## FDM Results - Flux Measurements Only



# Figure 31

## October 23, 1994 - Methane Concentrations (ppb) - 1 Metre Above Surface
## FDM Results - Flux Measurements Only



### *3.3.7 Determination of Methane Contribution from Point Sources*

Considering the significance that point sources contribute to the landfill emissions measured in comparison to that modeled from the surface flux data attempts were made to include point sources in the model to simulate the actual measured concentration. For example, a comparison of Figure 20 with Figure 28 shows that there is likely a point source contribution near S-25. In addition the measured ambient concentrations at S-22 and S-23 are much higher than the predicted concentrations.

An additional point source (0.5 g/s) was added in the vicinity of S-25 and an area source (9.6 g/s) in the vicinity of S-21. The model calculations were repeated with Figure 32 illustrating the result. Comparison with Figure 20 shows the adjusted emissions give much better agreement with the ambient measurements. The total $CH_4$ emission rate from the Keele valley Landfill is 11.5 g/s which is an increase of 88% from the emission rate based on the surface flux data alone. This increased emission rate is at most 2% of the potential $CH_4$ emission rate indicating an effective cover efficiency of at least 98%. For a more accurate estimate of the overall emission rate from the landfill this type of analysis would have to be done across the whole landfill.

### *3.3.8 Landfill and Natural Gas Distribution Centers Perimeter Runs*

Three Perimeter runs around each the landfill and the natural gas distribution centre were conducted over a four day period. An example can be found in Figures 33 below and Figure 34 on the next page which show the perimeter route and corresponding ambient methane measurements 4 meters above the surface around the Keele Valley Landfill conducted on September 28, 1993.

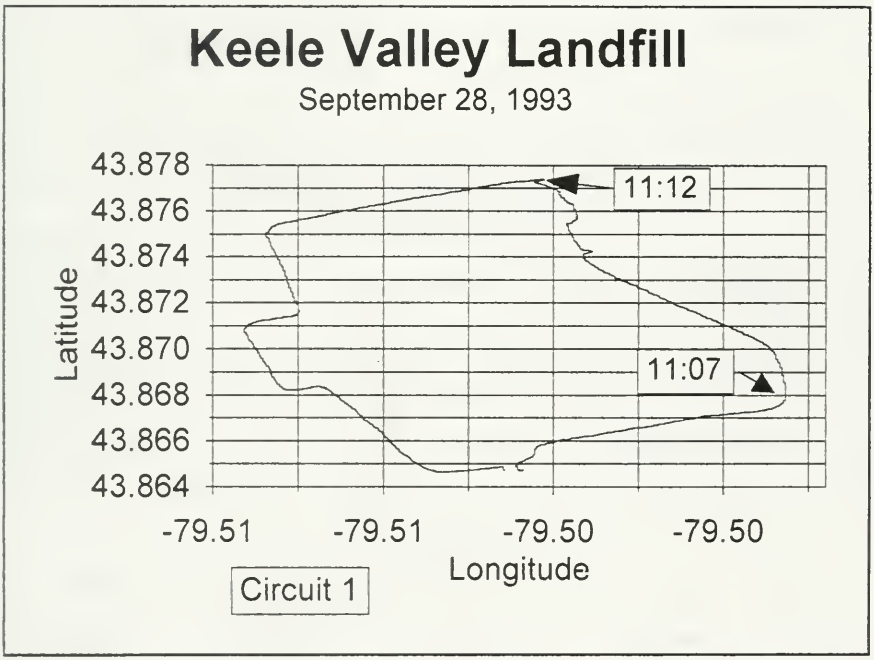



Figure 33 Mapping of Keele Valley Landfill Perimeter run 2

Note in the ambient measurement figure below the peak values occur at the eastern side of the haul road. The relatively wide plume agrees with the weak southeasterly wind measured this day. Similar perimeter runs around the TransCanada compressor station showed plume levels of about 5 ppmV of various widths. Although these measurements indicate both these sites as sources of methane, concentrations significantly above background were measured only on the landfill and distribution center property. Further downwind runs (distances from .5 to 5 km) showed no statistical evidence that any increase in Methane above background are from these two sources. Vehicle exhaust or other anthropogenic sources may override these sources to the extant that no plume was detected.

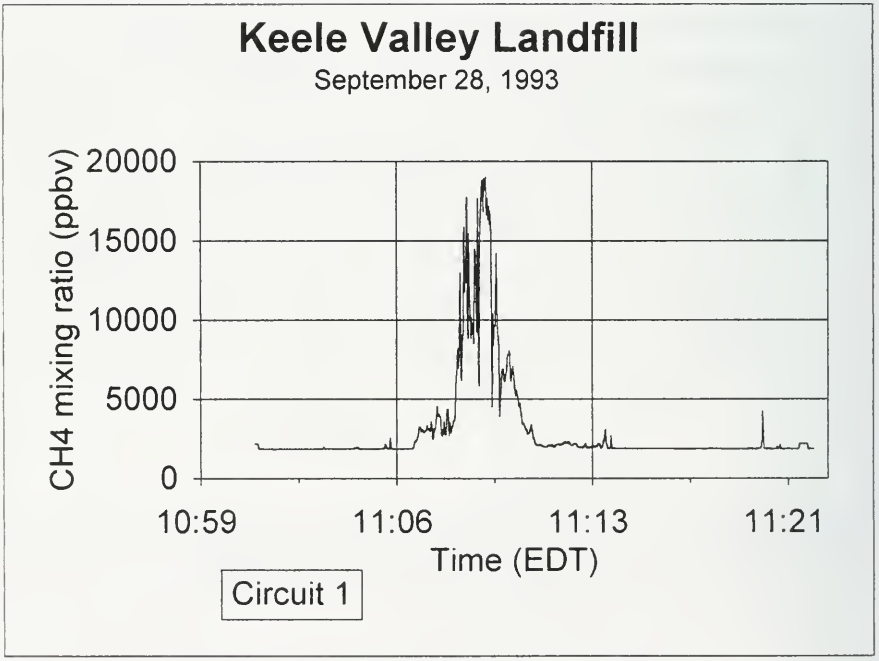



Figure 34 Ambient $CH_4$ Measurements for KVL perimeter run 2

The Fugitive Dust Model was used to determine the methane contribution from the landfill at receptors depending on meteorological conditions placed on Dufferin Street, Major Mackenzie Drive, Keele Street and Rodinea Road. The Methane sources were modeled using the experimentally derived estimated emission rates. None of the receptor locations indicated methane concentrations greater than 100 ppbv above minimums which were taken as background. These observations were verified by the modeled results. Just how significant this is would require more downwind plume measurements at higher altitudes.

### *3.3.9 Landfill Surface Mapping*

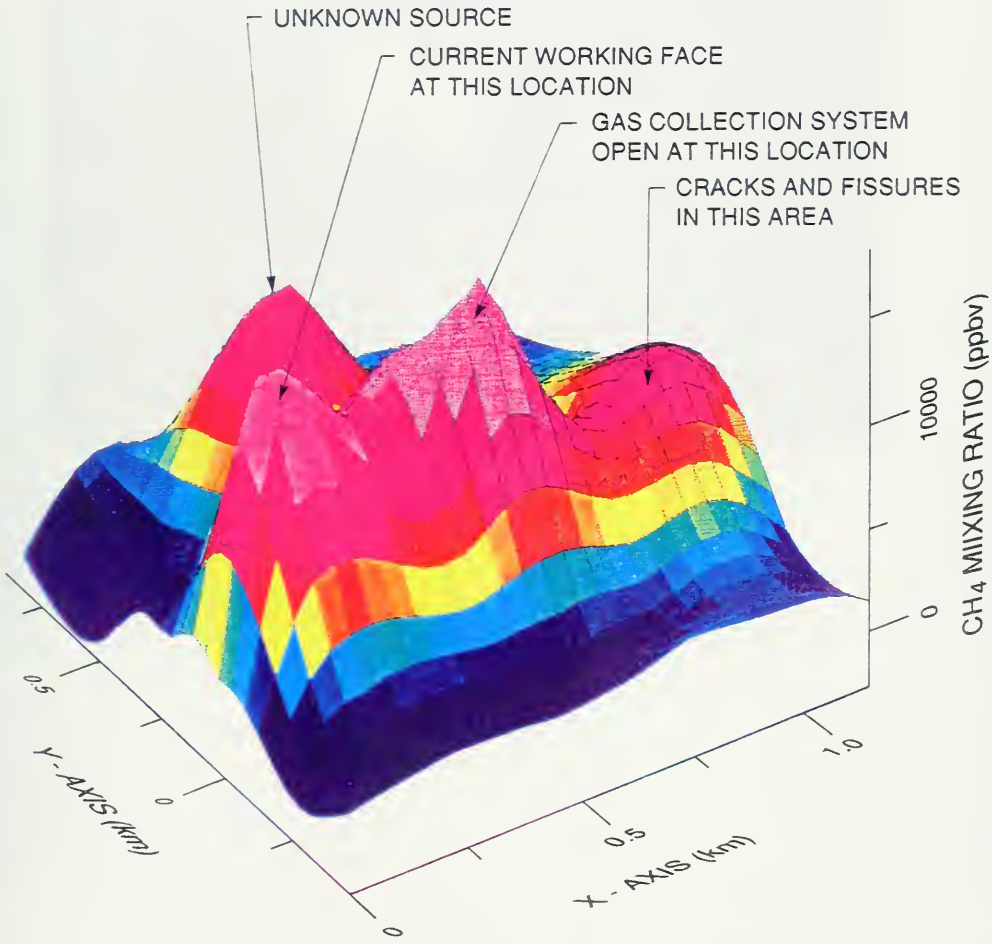
Refer to Figure 36 which is a surface plot of the Keele Valley Landfill for October 6, 1994. This day was chosen as half the sections were sampled utilizing the procedure outlined in section 3.1 with five minute averages, the rest of the points were 2 minute averages only. This was done to have a sample set of the whole landfill taken in just one day and time would not permit a data set entirely of five minute averages. Although this may bias the surface plot in some manner this exercise was only done to illustrate how this technology can point out local hot spots. This surface plot shows the point to point variability that applies to the emission of methane at a landfill with four areas of much higher emissions clearly indicated. This was the only complete one day mapping of the Keele Valley Landfill as subsequent data sets were over a period of two days.

## 3.4 Summary Second Year Effort

Over 150,000 field measurements of methane and ethane were made over the second period of this project. Refer to Photograph II showing the instrument on location. Successful mapping and modeling of the Keele Valley Landfill indicated that surface flux measurements from flux chambers over this sampling period account for only one-fifth of the total emissions at this site. The rest of the gaseous emissions arise from either point or area sources. The flux chamber method of analysis will only obtain the flux of $CH_4$

through the surface and not account for these other significant sources. Each flux chamber measurement on average took one hour to complete. To do a proper statistical survey of the entire landfill utilizing the flux chamber methodology would take a few weeks or more. We have shown that the entire landfill can be mapped by the TDLAS at one height in just one day. The TDLAS methodology has also shown that it has the advantage of detecting both the surface flux component and the point source component. The point source or area source component being more significant at this site. From only the perimeter run measurements of the pipeline distribution center the emission rates of methane from the Keele Valley Landfill (11.5 g/s) appear to be at least a factor of six higher than that from the Maple TransCanada PipeLines distribution center (< 2 g/s). This result is quite speculative as not enough measurements were made at each site to pass statistical confidence tests and is included only as a preliminary result. The perimeter run data one to five kilometers downwind from these two sites indicate that ambient methane was only minimally increased. The modeled results from the flux chamber data were not in agreement with the measured ambient methane mixing ratios. Increased agreement between the modeled and measured results occurred once a few point sources were incorporated into the model. Model runs for one to five kilometers downwind of the two source sites agreed with ambient measurements.

# METHANE EMISSIONS MEASURED ONE METRE ABOVE THE SURFACE AT KEELE VALLEY LANDFILL OCTOBER 6, 1994

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# MEASUREMENTS ON LOCATION PHOTOGRAPH 2

## 4.0 CONCLUSIONS

The TDLAS methodology as applied to the measurement of $CH_4$ at both a landfill and a natural gas distribution center has shown that it is a highly sensitive technique as good or better than any other available method. We have shown in the lab that the TDLAS technique provides high spectral resolution and absolute identification of the two species (methane and ethane) measured during this project. From the field measurement program the analysis of the results clearly shows that this methodology is more economical and by far more comprehensive than that of flux chamber measurements alone. The modeling exercise utilizing this data set has shown that with a combination of surface flux measurements and ambient measurements a significant amount of insight into landfill and natural gas distribution centers $CH_4$ emissions can be achieved.

## 5.0 RECOMMENDATIONS FOR FUTURE WORK

The following recommendations for future work will be divided into two subsections, that concerning landfill measurements, the other concerning natural gas distribution and pipeline measurements.

### 5.1 Landfill Recommendations for Future Work

1) Using the same method build a larger statistical data base in mapping the landfill for methane based on ambient concentration measurements. Using the Fugitive Dust Model, the emissions from all regions of the landfill would be analyzed in conjunction with the ambient measurements to better estimate both the area specific as well as the overall emission rates from the landfill.

2) Apply this measurement program to other landfills for a comparison of results.

3) Develop a box model to convert ambient concentrations collected at 10 cm and 1 meter above the landfill surface into estimated fluxes from different areas of the landfill. There are already two complete data sets of the Keele Valley Landfill to do initial model runs of this type.

4) Design a time scaled boom to include $CH_4$ measurements at different altitudes during downwind perimeter runs, this would enable us to detect the altitude component of the methane plume.

5) Intercompare the TDLAS with our developed LASAIR technique. This technique is described in Appendix B. The LASAIR would permit faster scanning of the landfill and is a portable unit.

6) Using new ambient measurements to better identify, quantify and locate point source emissions across the landfill and make observations concerning their mitigation.

## 5.2 Natural Gas Distribution Centers Recommendations for Future Work

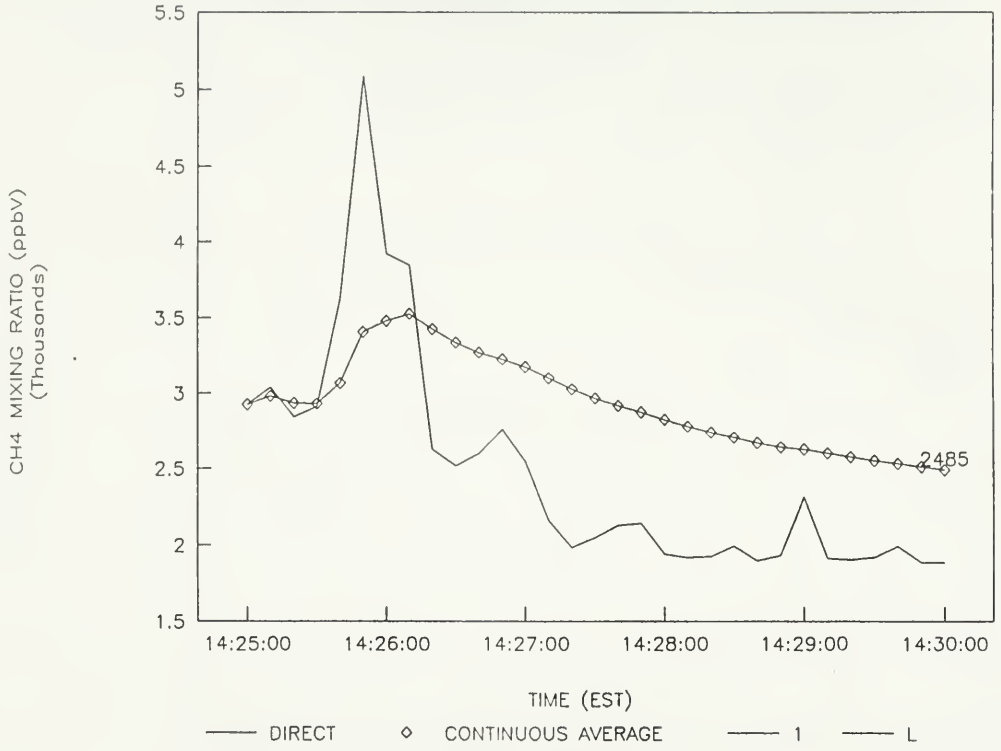
1) Since we were unable to measure any ethane above background levels due to limited access and the strong likelihood that there were no appreciable leaks on the days we sampled, we suggest that a leak be generated for us. This would permit measurements of the methane/ethane ratio at various distances downwind of the known leak.

2) Attempt to use the LASAIR technology to monitor the same leak as mentioned above.

# APPENDIX A

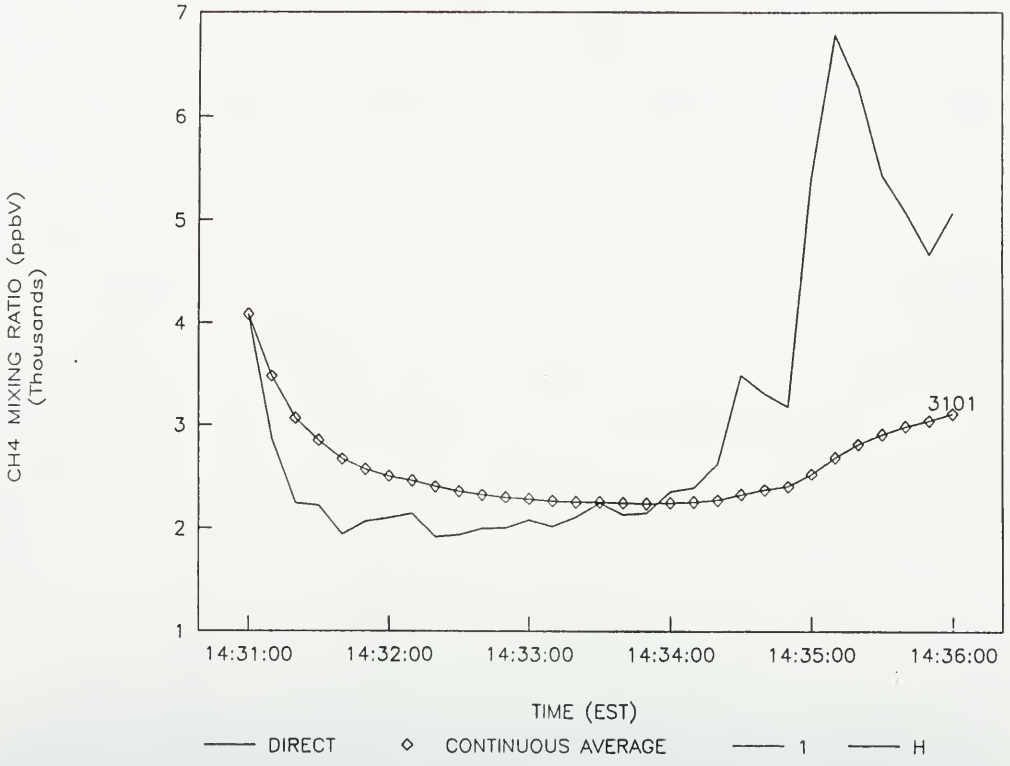
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



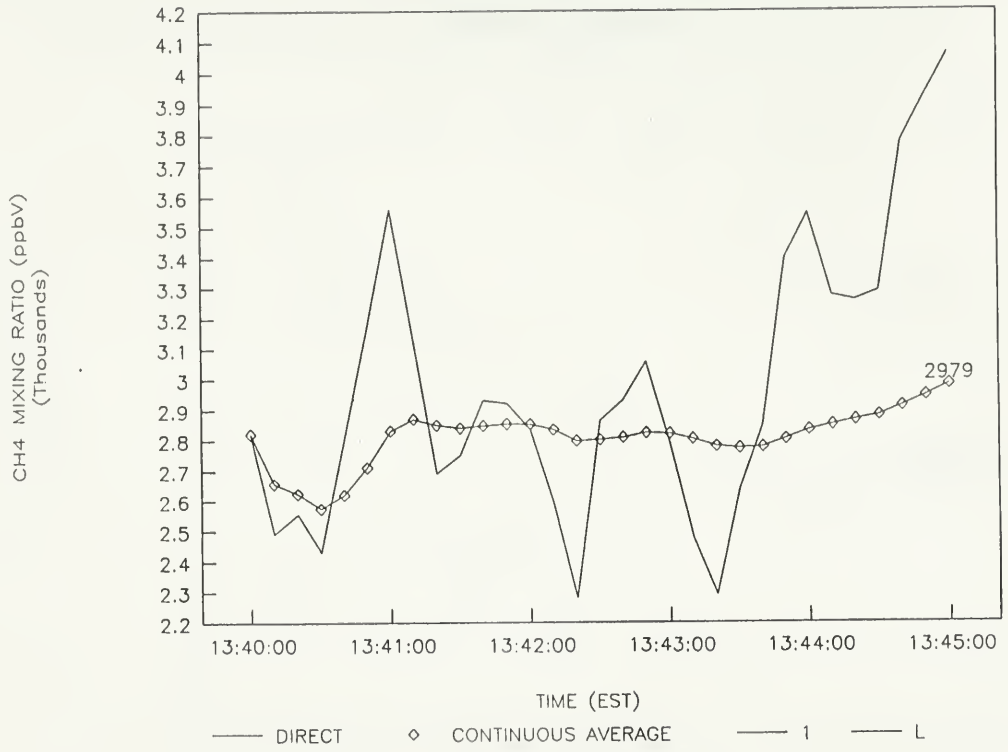
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



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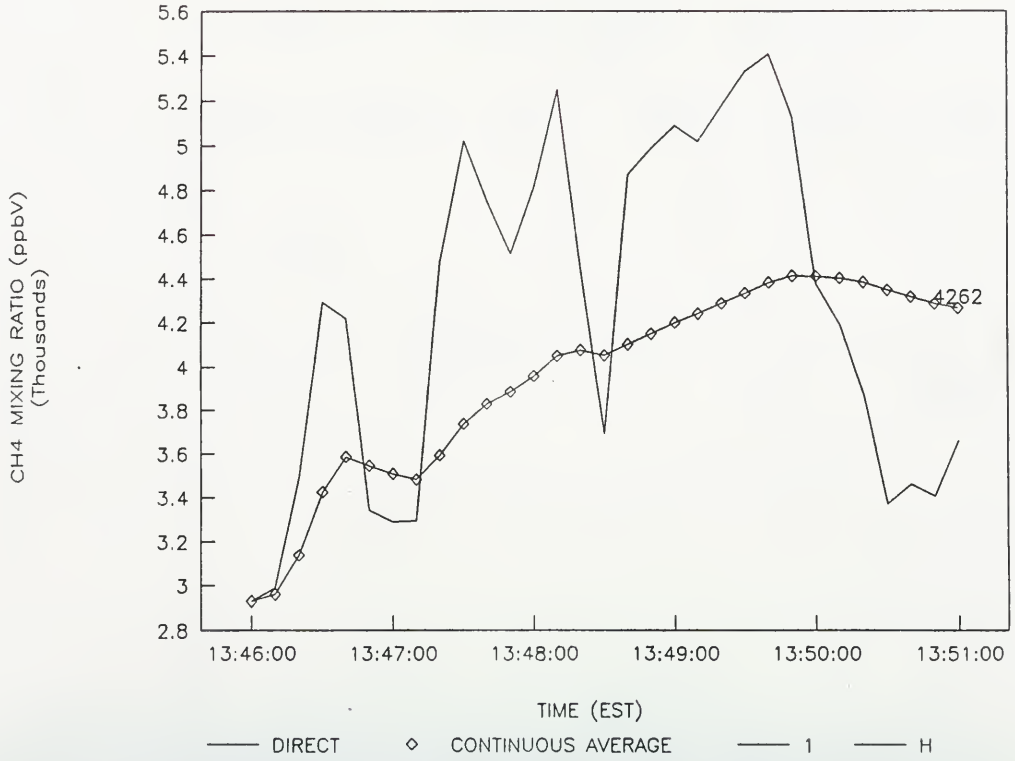
DATE : OCTOBER 12, 1994



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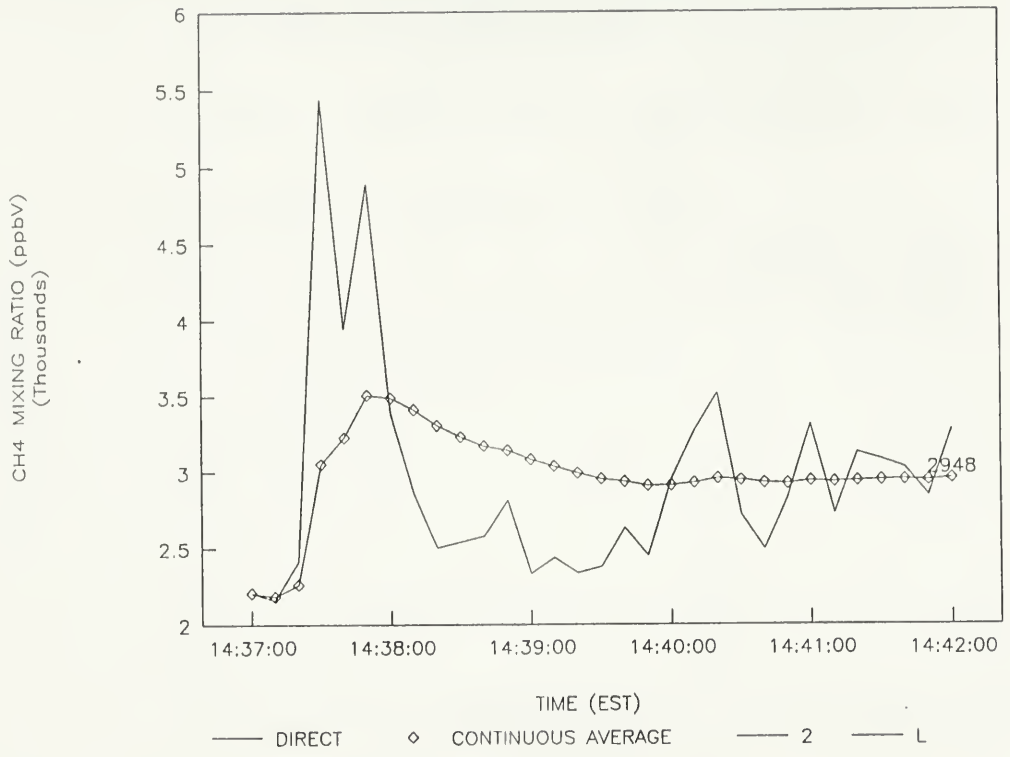
DATE : OCTOBER 6, 1994



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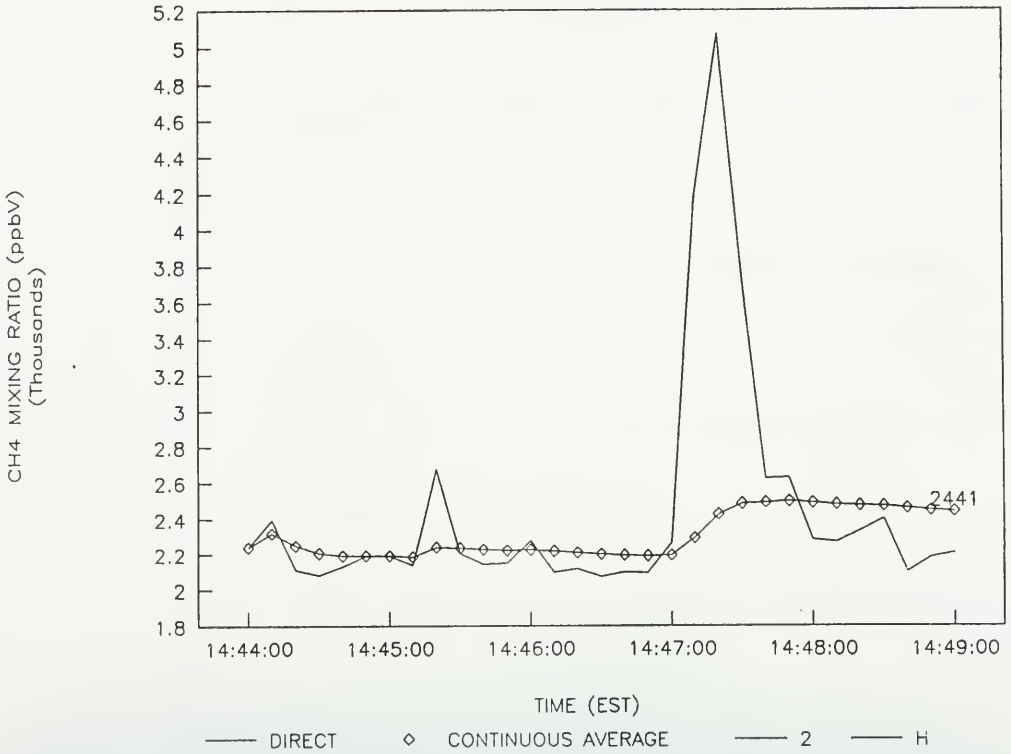
DATE : OCTOBER 6, 1994



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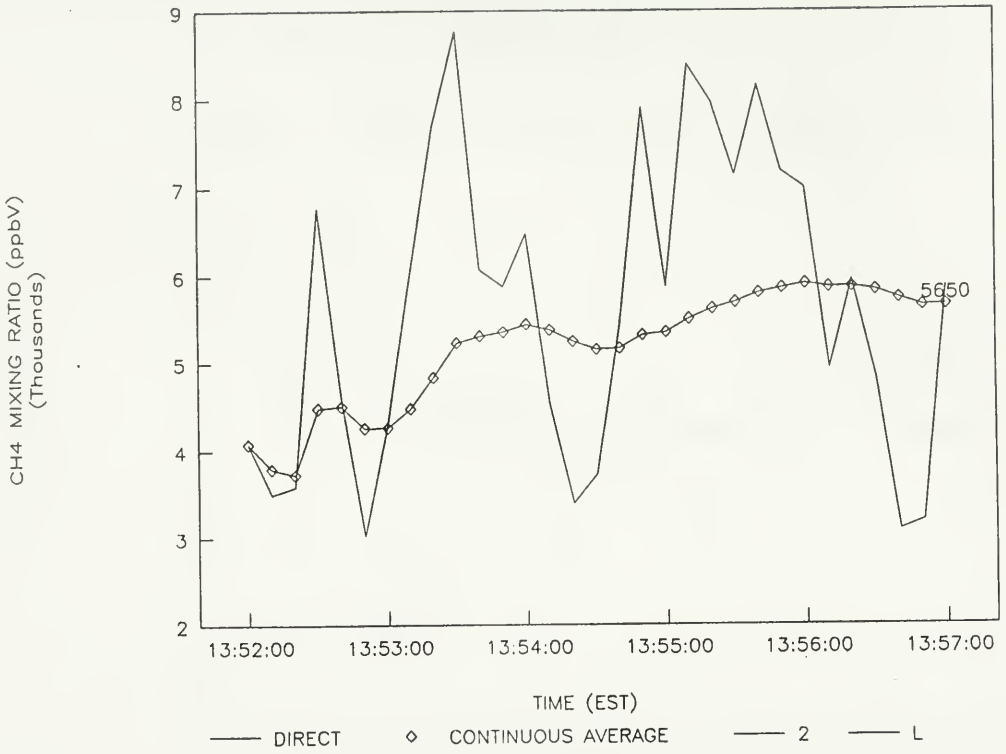
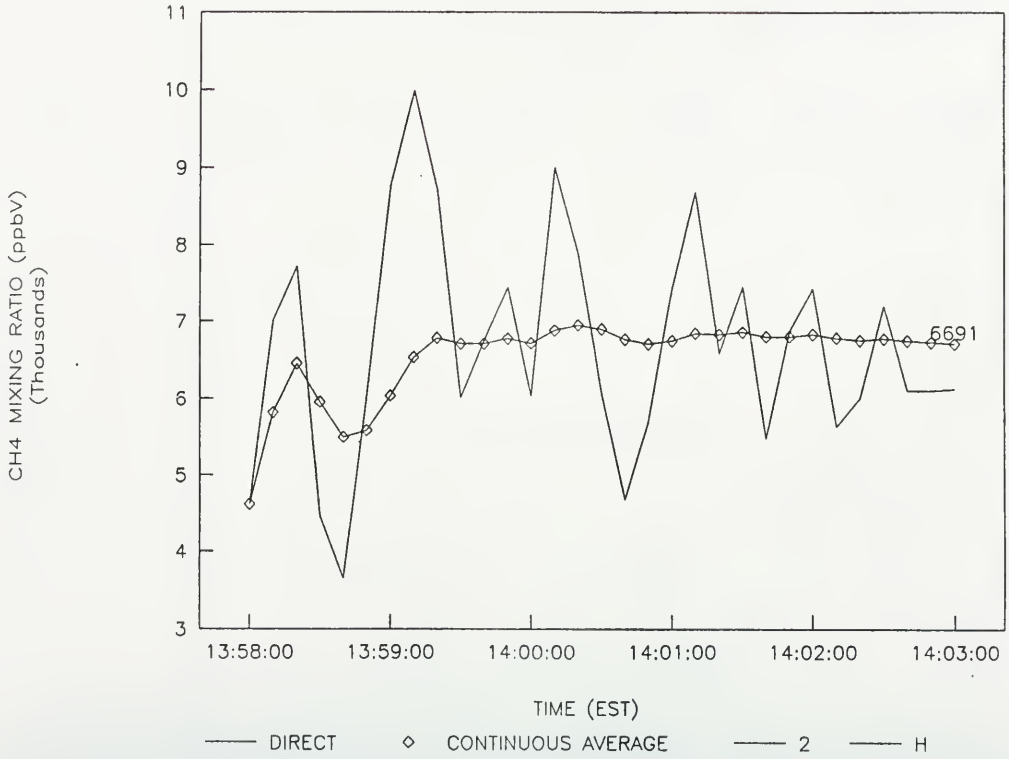
DATE : OCTOBER 12, 1994



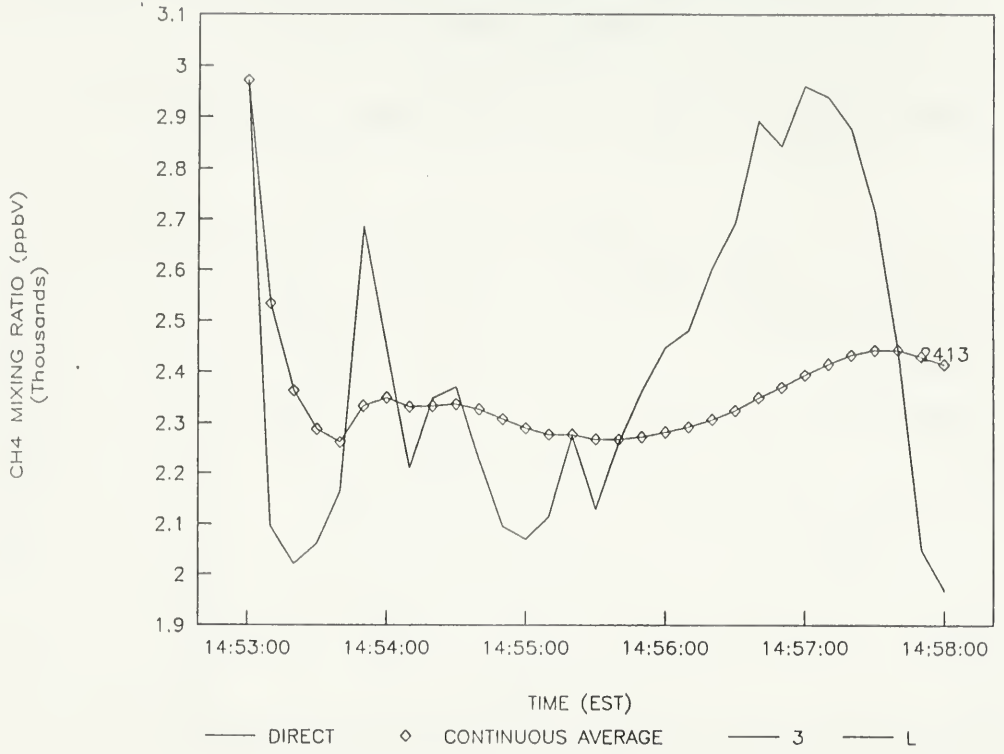
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



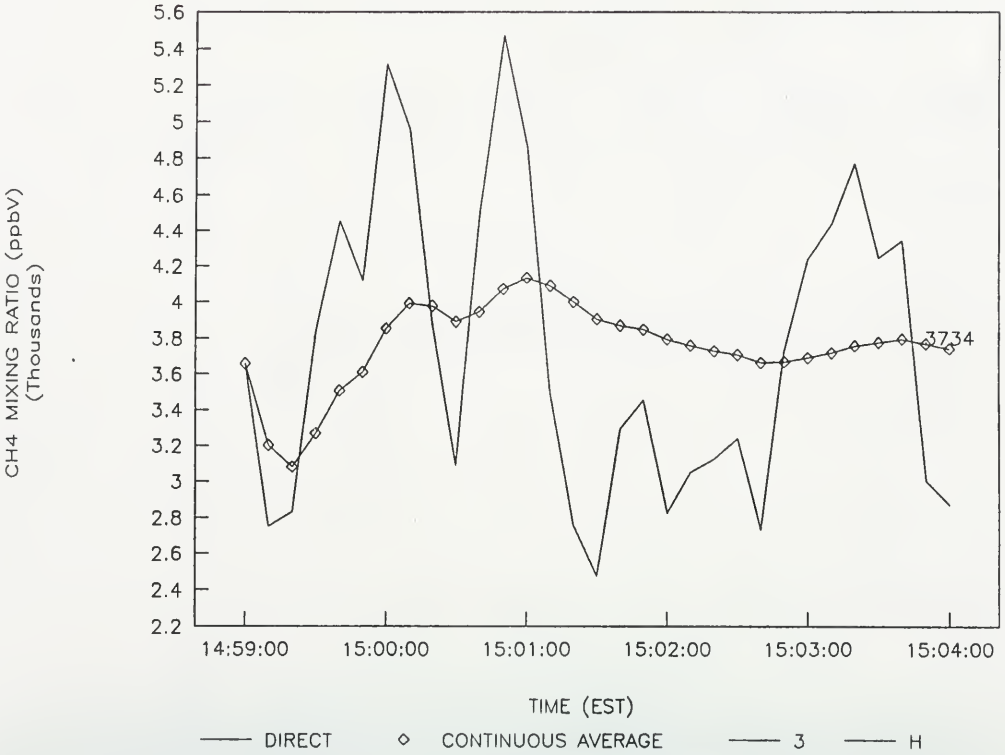
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



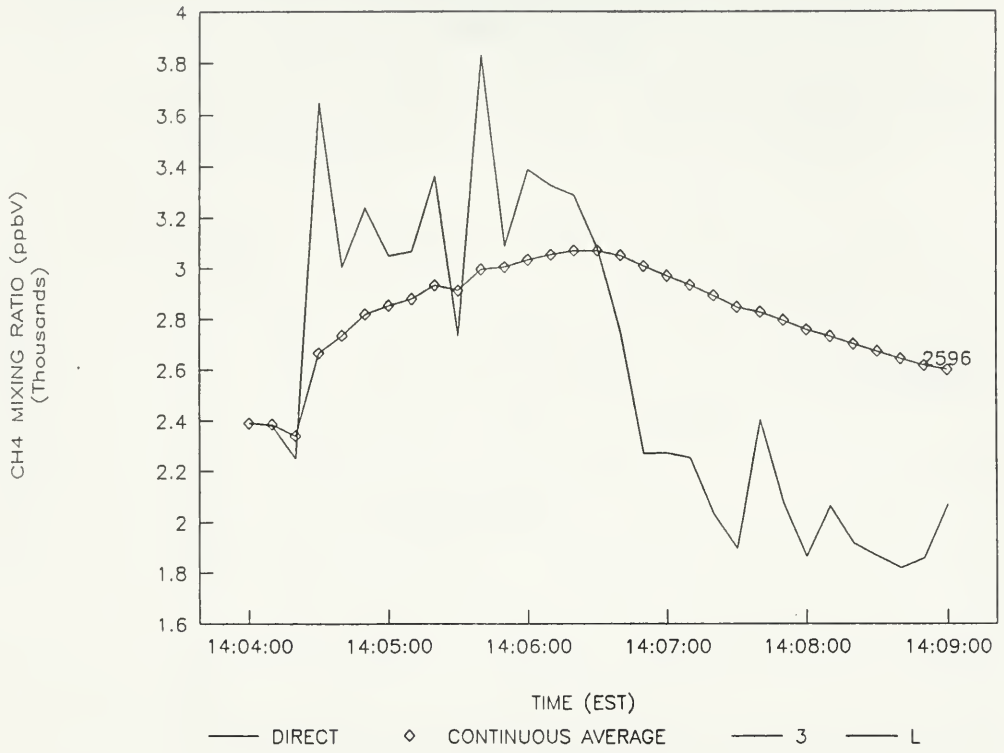
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



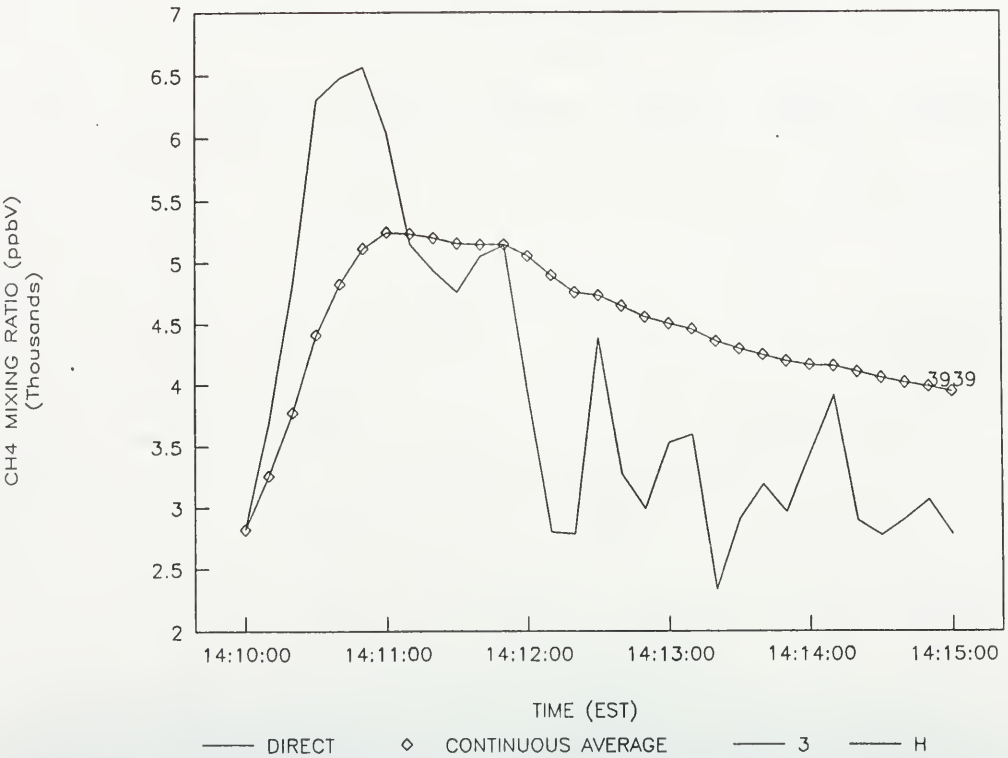
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



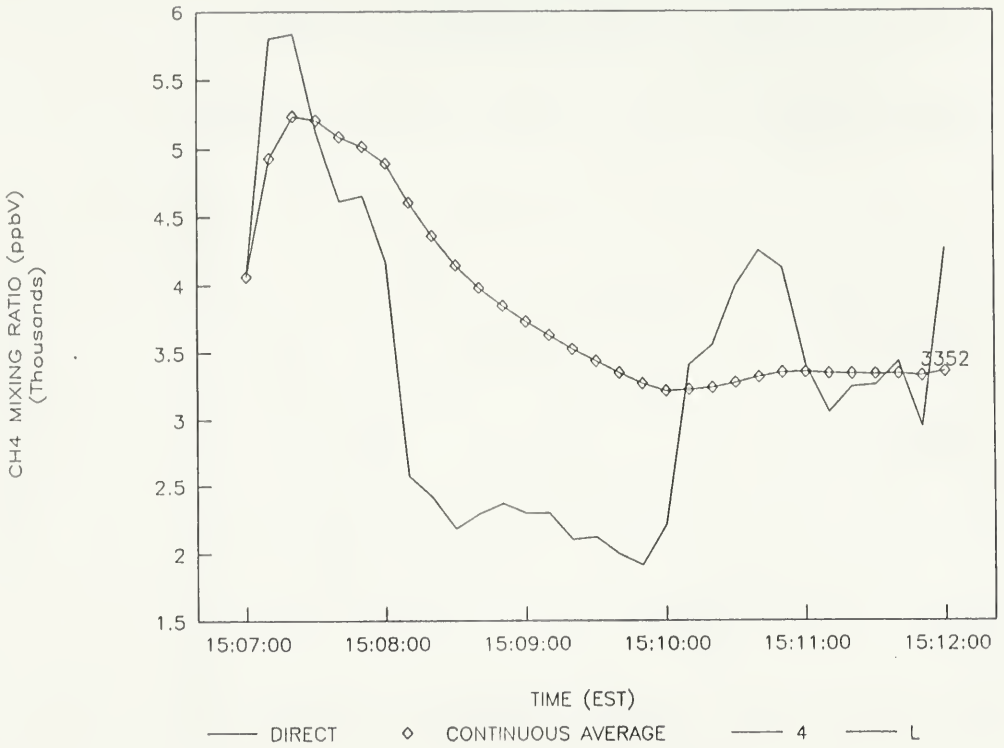
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



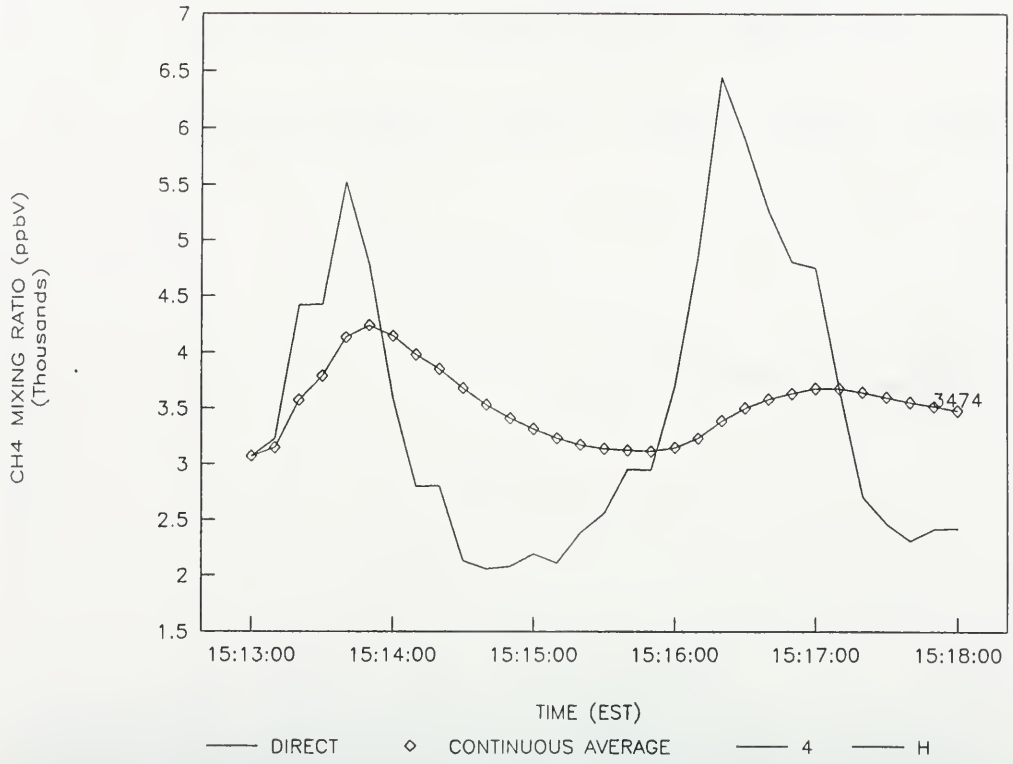
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



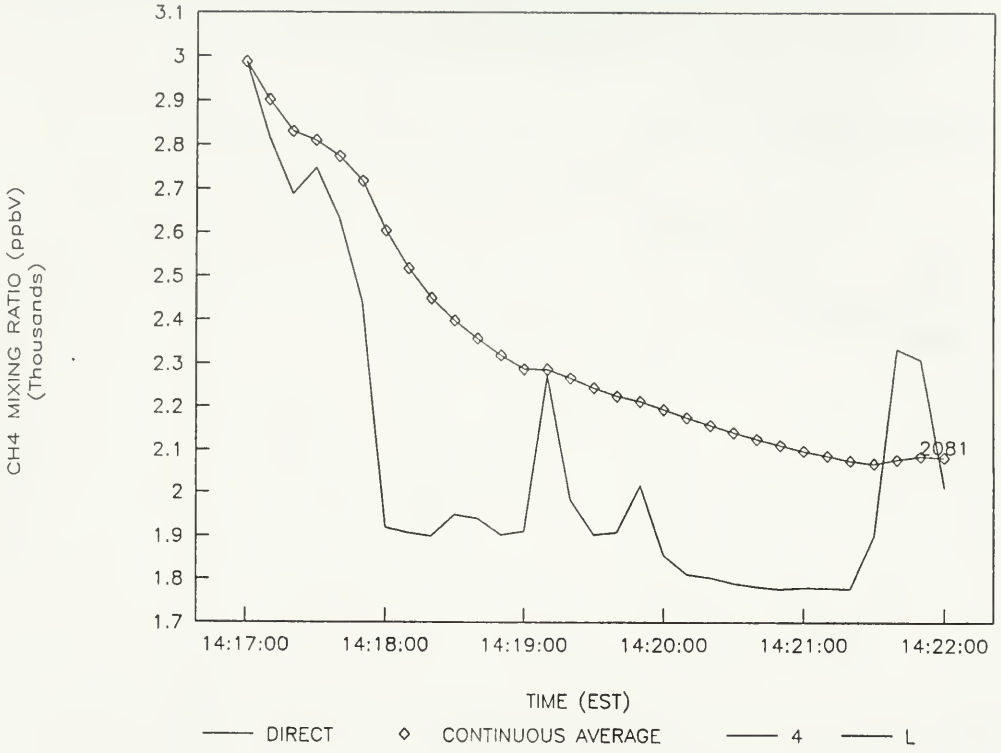
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



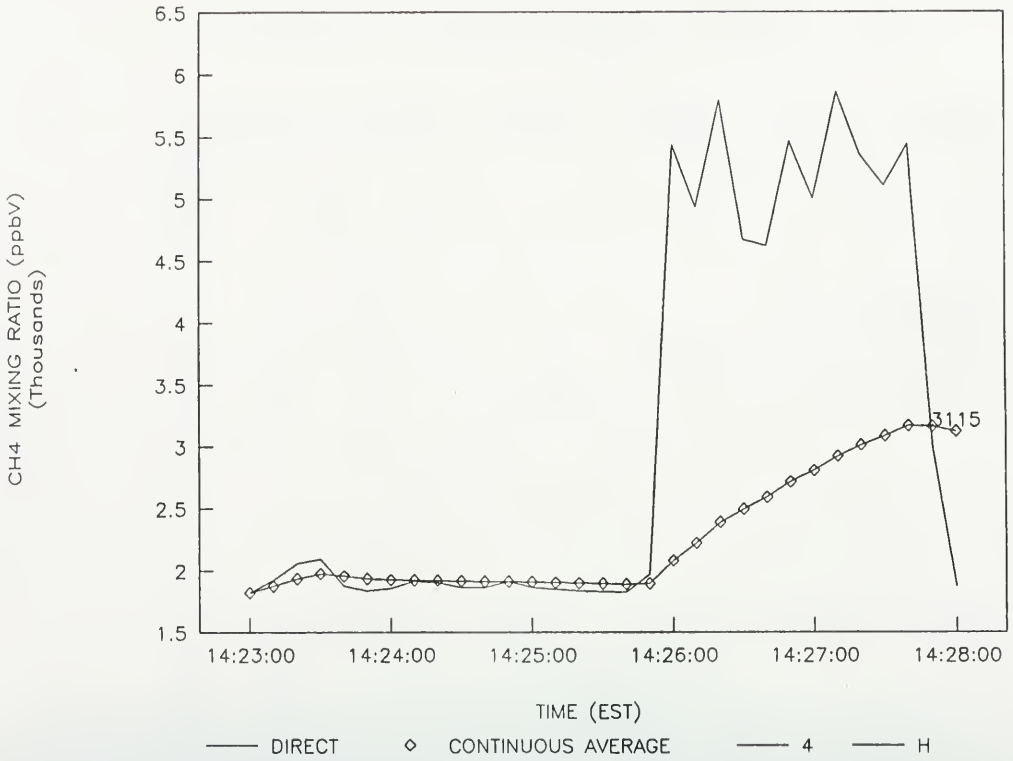
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



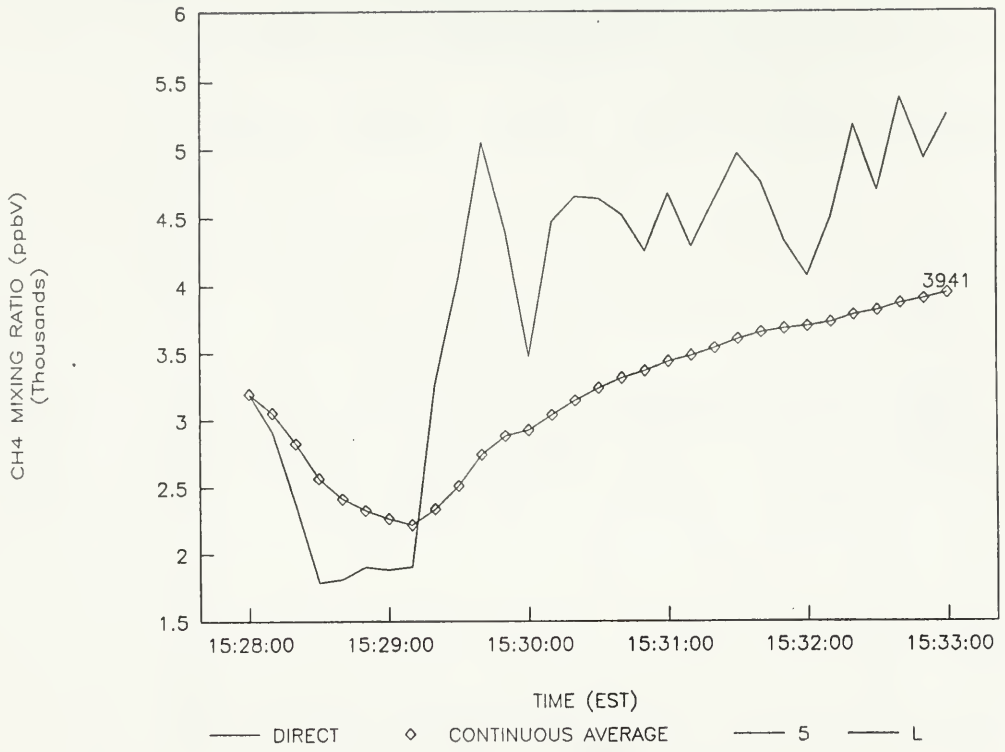
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



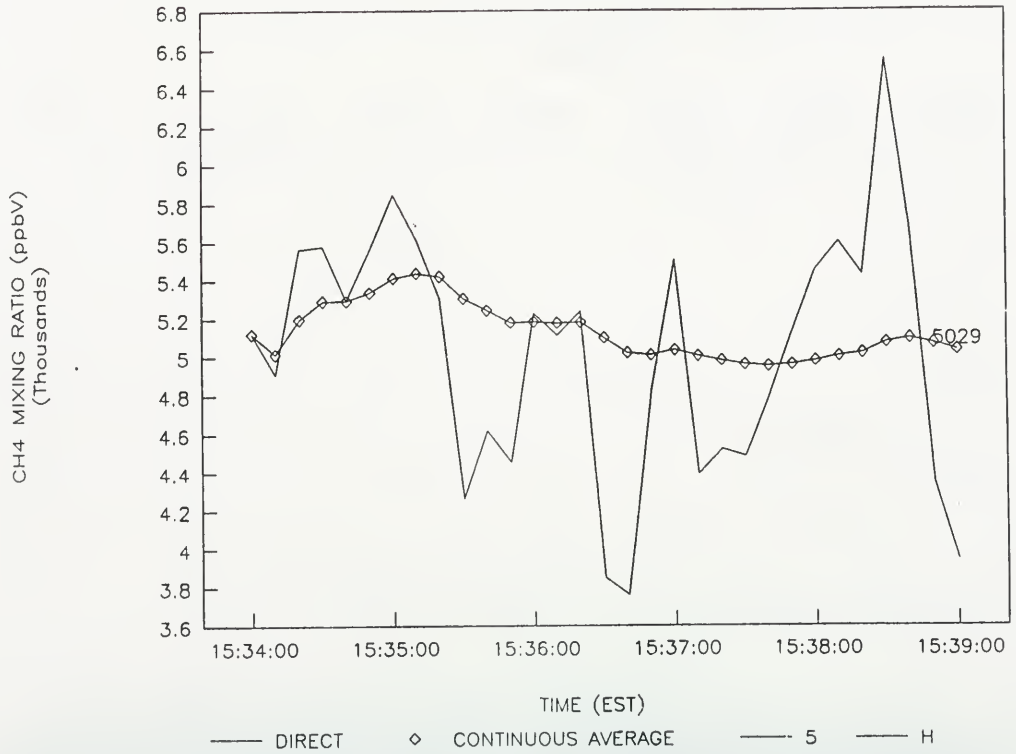
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



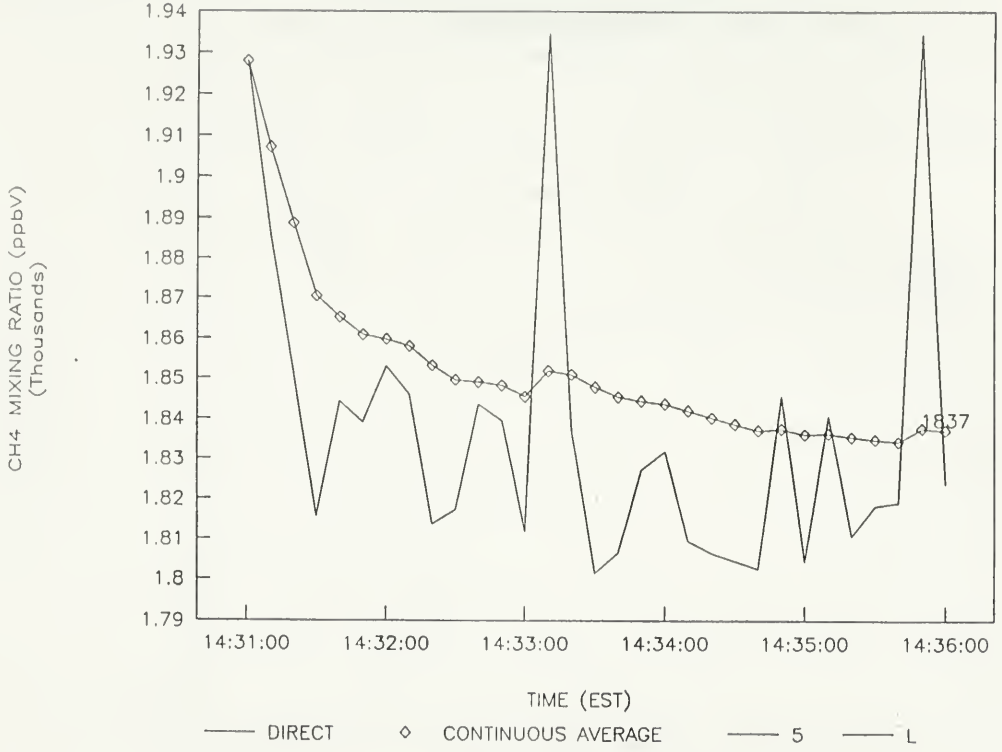
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



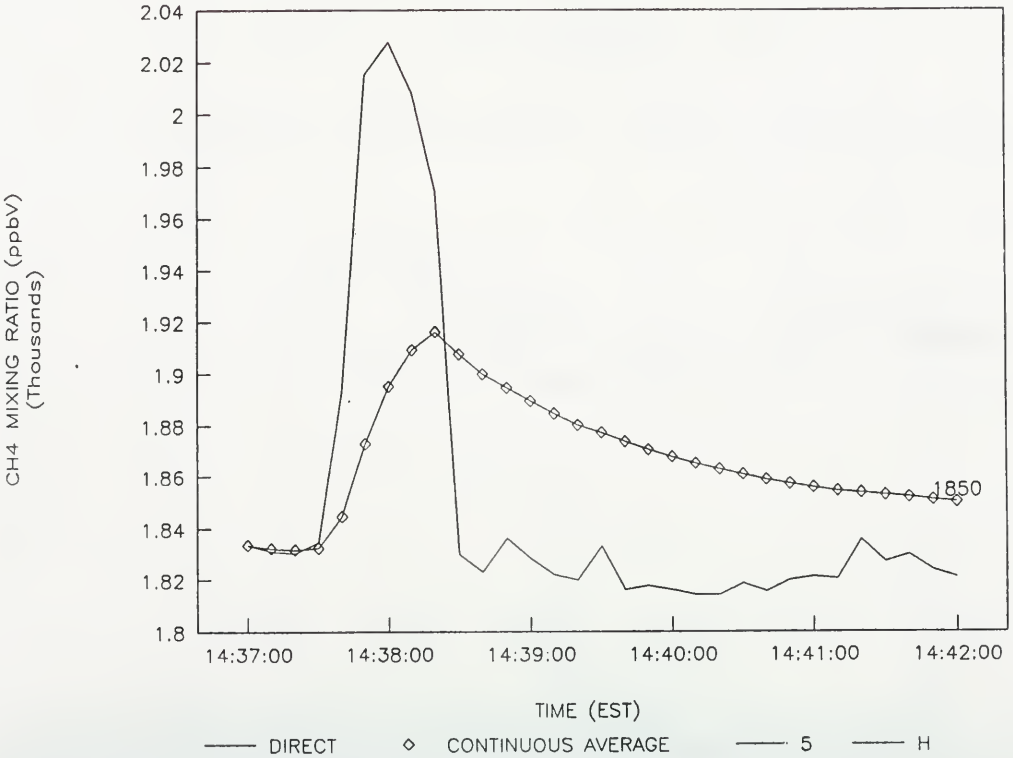
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



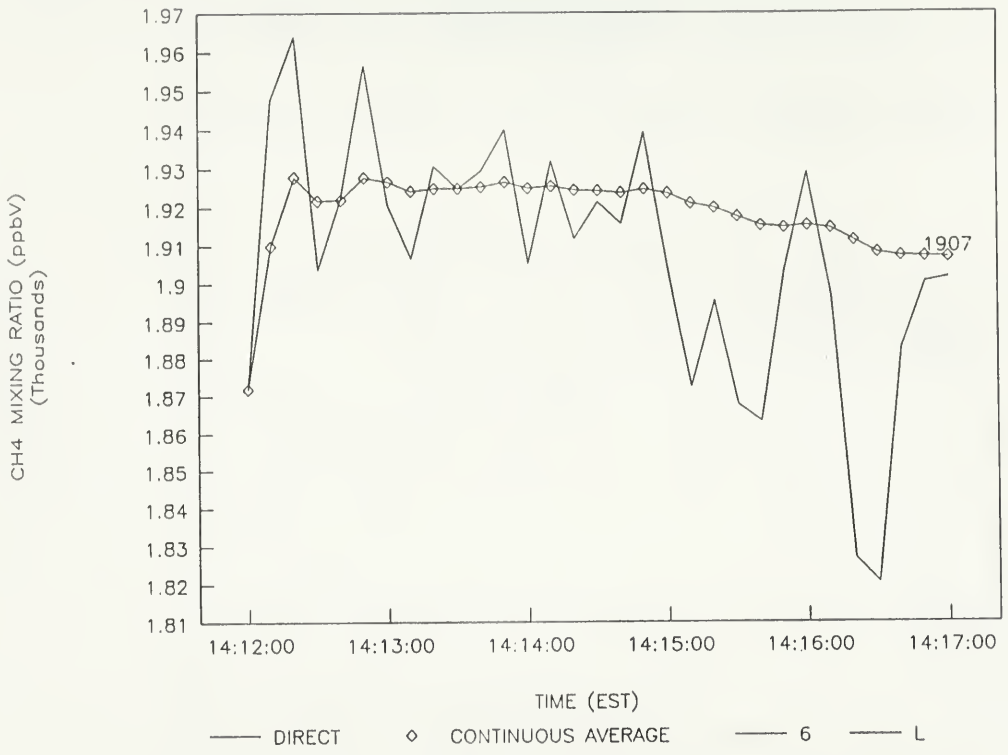
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



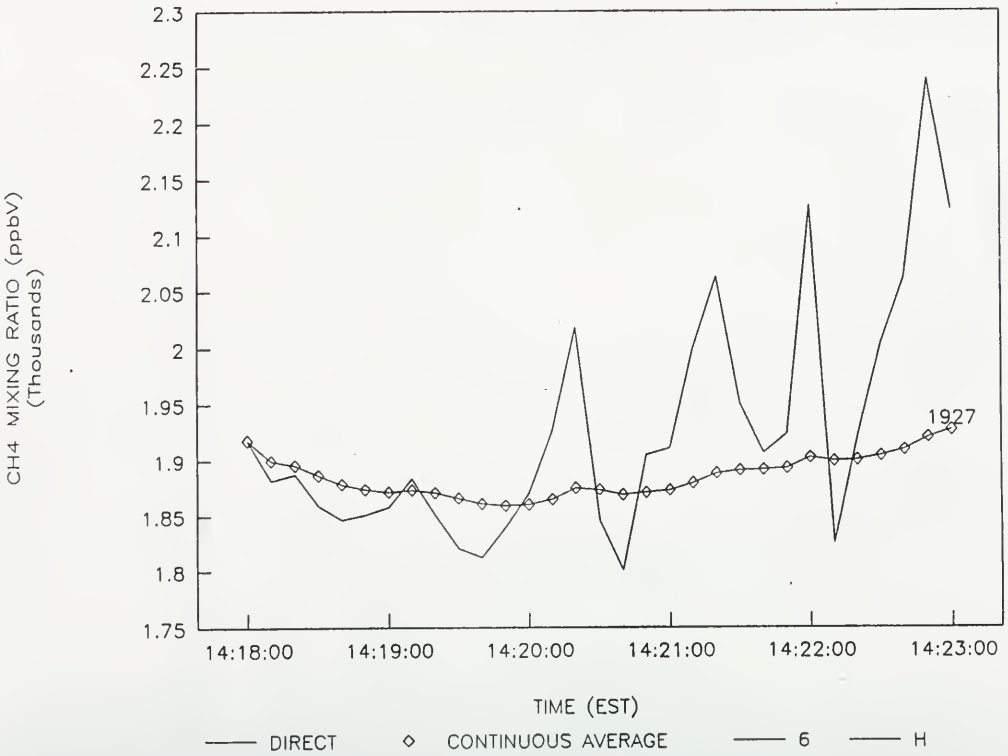
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



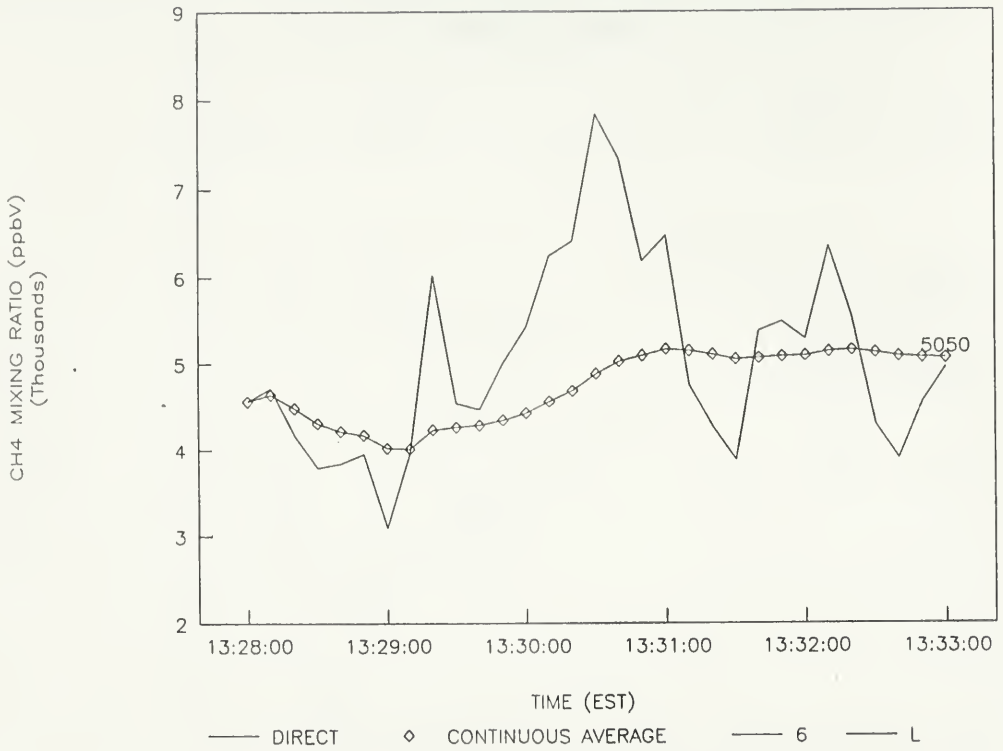
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



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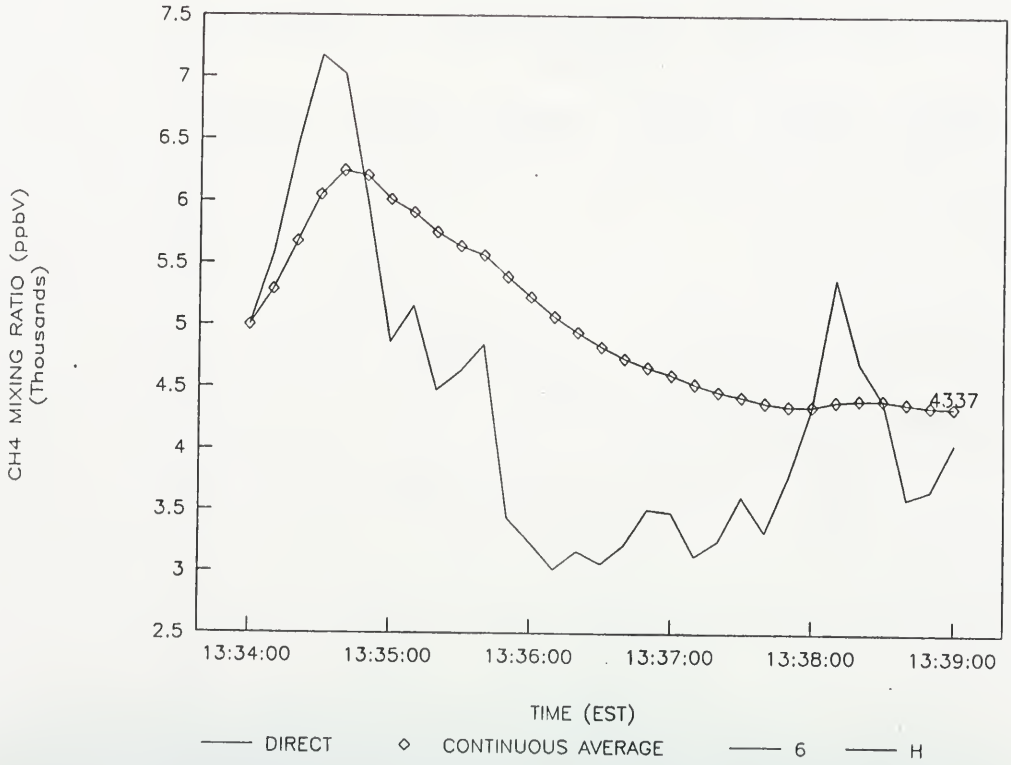
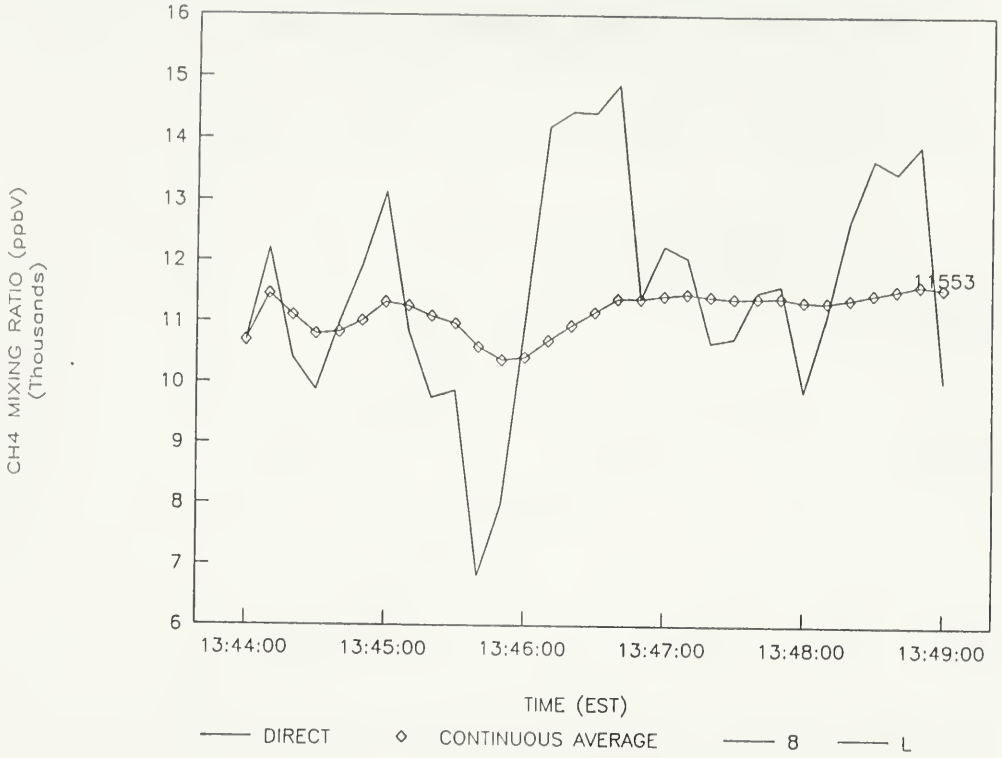
DATE : OCTOBER 12, 1994



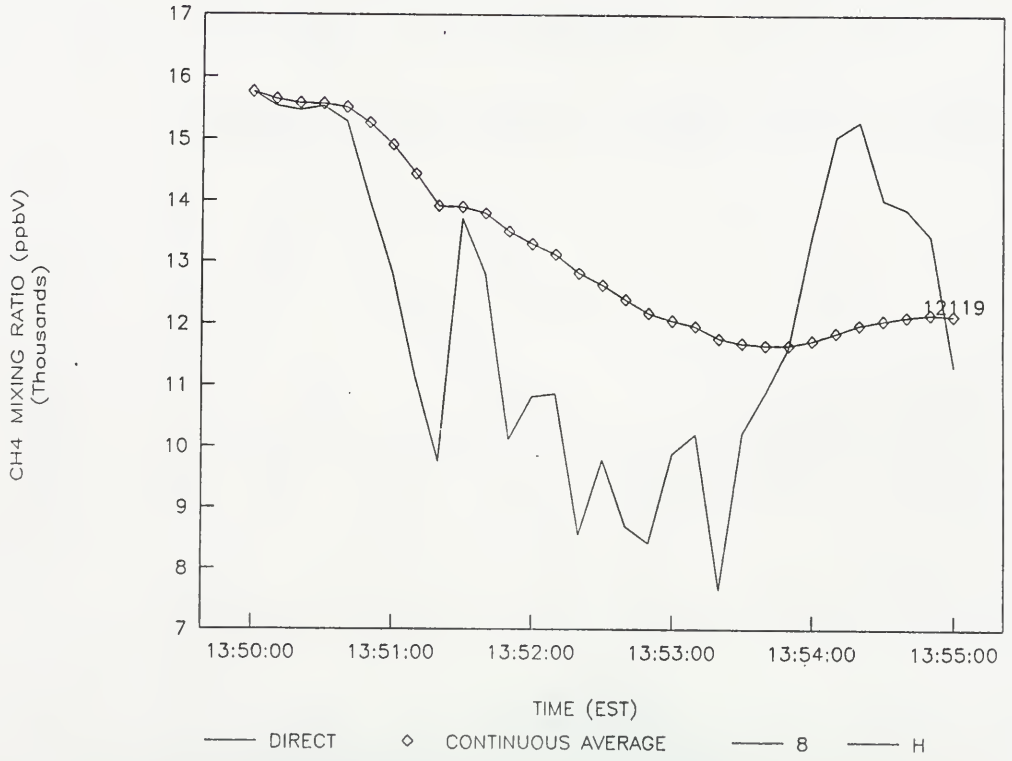
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 7, 1994



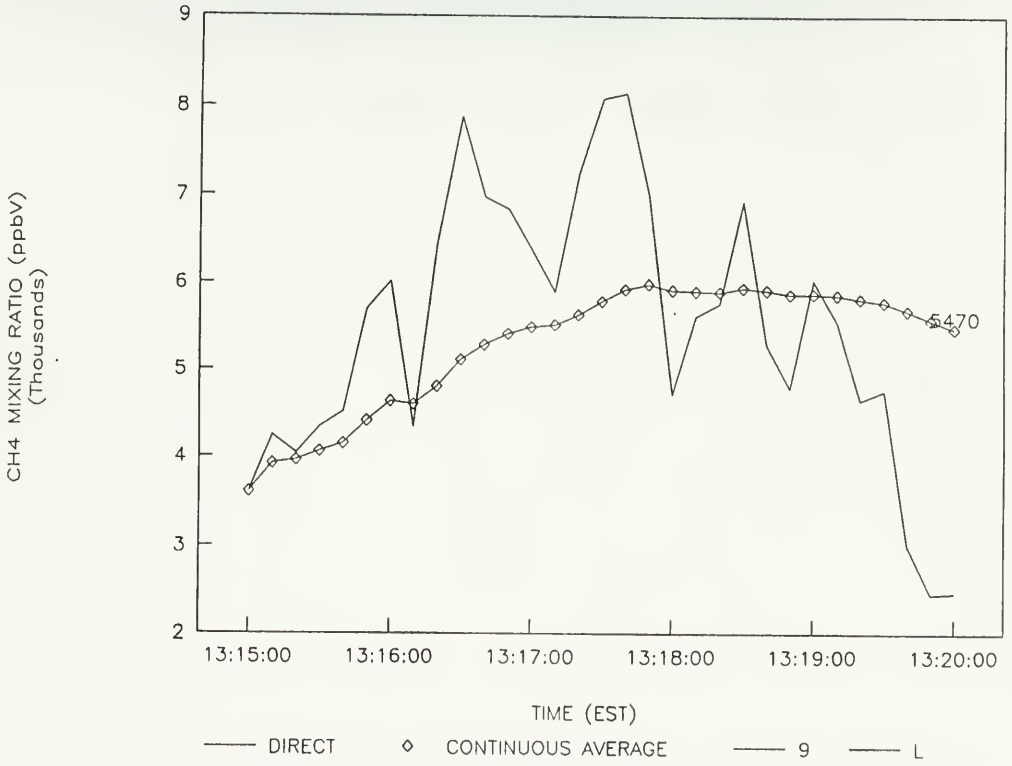
# KEELE VALLEY LANDFILL CH4 STUDY

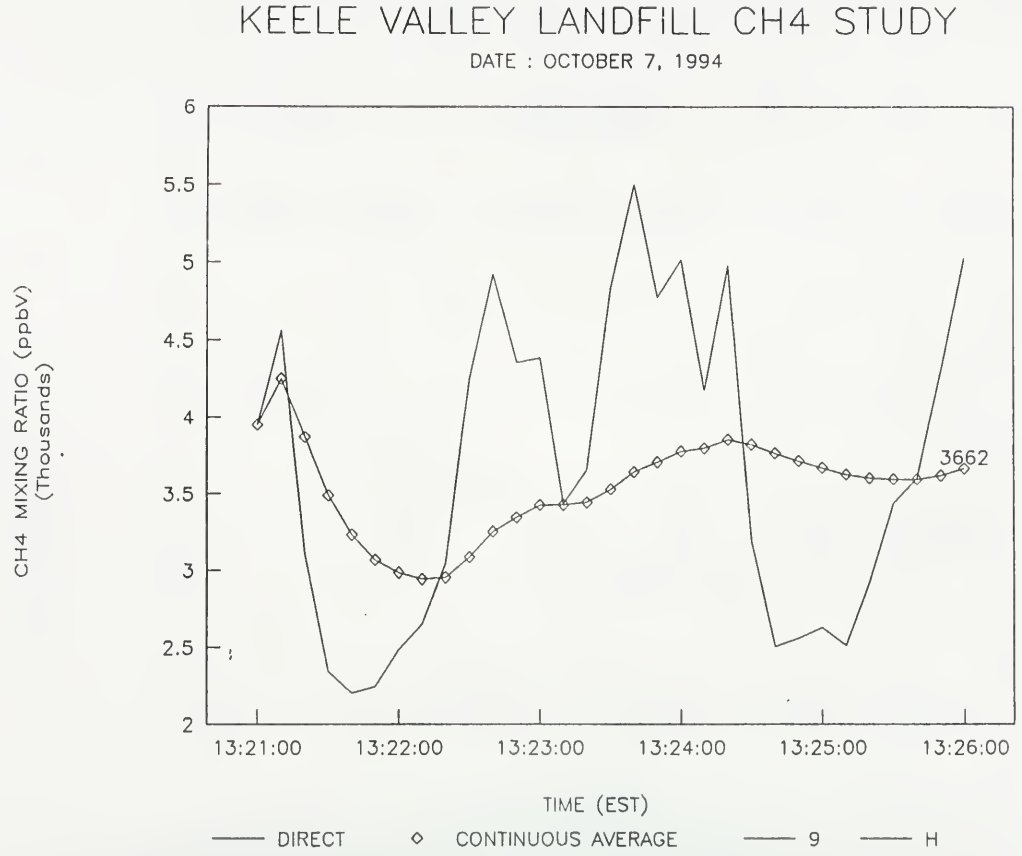
DATE : OCTOBER 7, 1994



# KEELE VALLEY LANDFILL CH4 STUDY

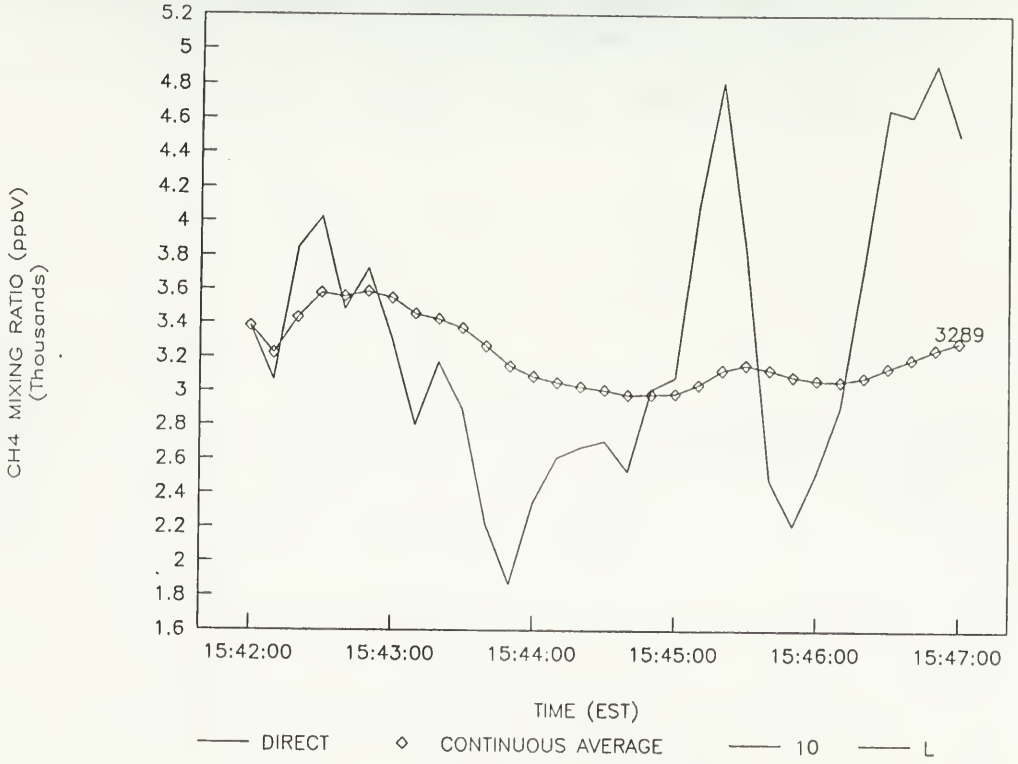
DATE : OCTOBER 7, 1994

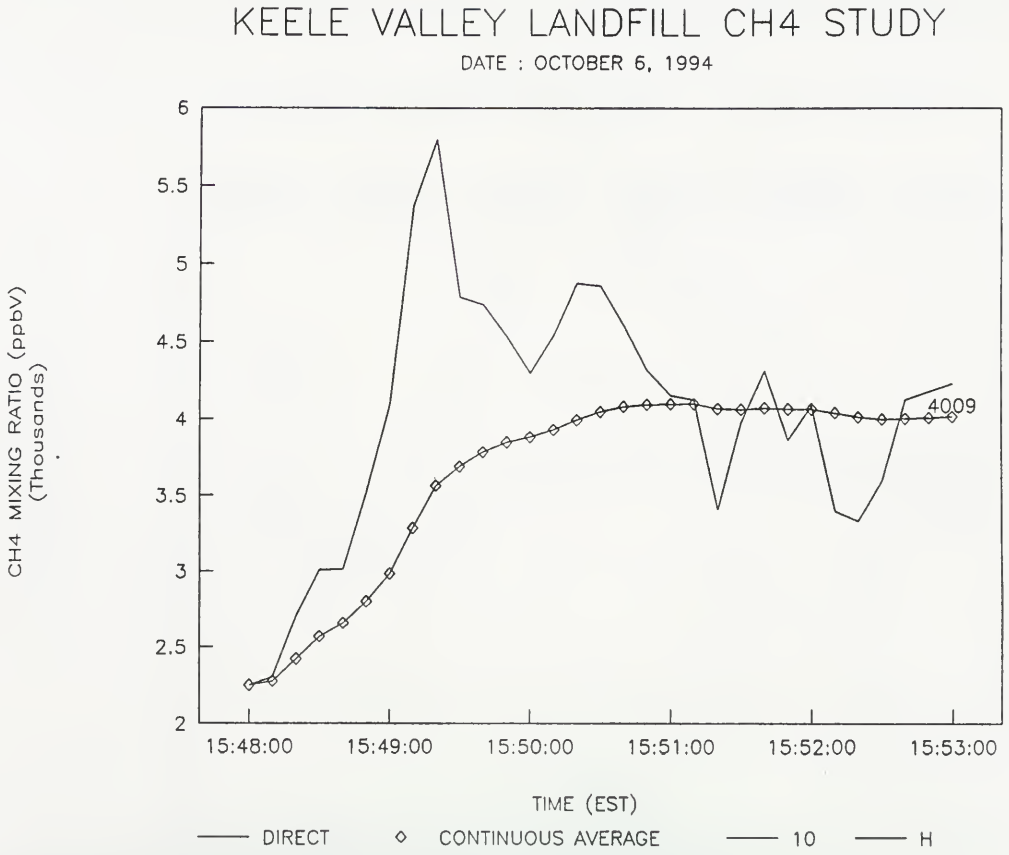



KEELE VALLEY LANDFILL CH4 STUDY
DATE : OCTOBER 7, 1994
CH4 MIXING RATIO (ppbV)
(Thousands)
6
5.5
5
4.5
4
3.5
3
2.5
2
3662
13:21:00
13:22:00
13:23:00
13:24:00
13:25:00
13:26:00
TIME (EST)
DIRECT
CONTINUOUS AVERAGE
9
H

# KEELE VALLEY LANDFILL CH4 STUDY

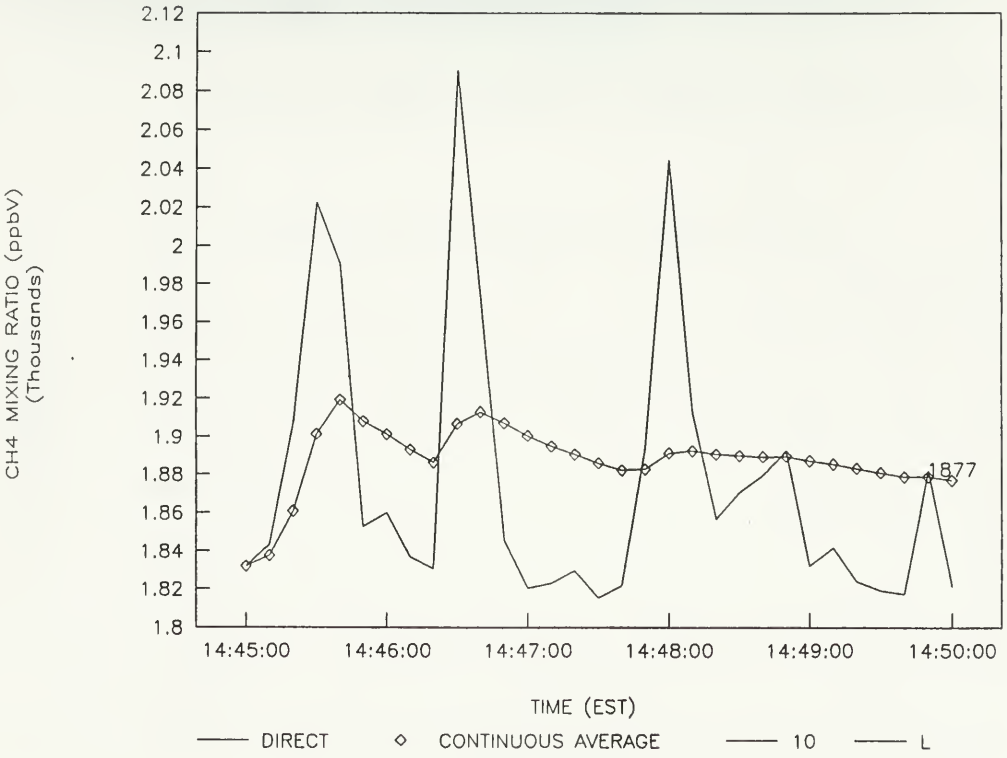
DATE : OCTOBER 6, 1994




KEELE VALLEY LANDFILL CH4 STUDY
DATE : OCTOBER 6, 1994
CH4 MIXING RATIO (ppbV)
(Thousands)
6
5.5
5
4.5
4
3.5
3
2.5
2
4009
15:48:00
15:49:00
15:50:00
15:51:00
15:52:00
15:53:00
TIME (EST)
DIRECT
CONTINUOUS AVERAGE
10
H

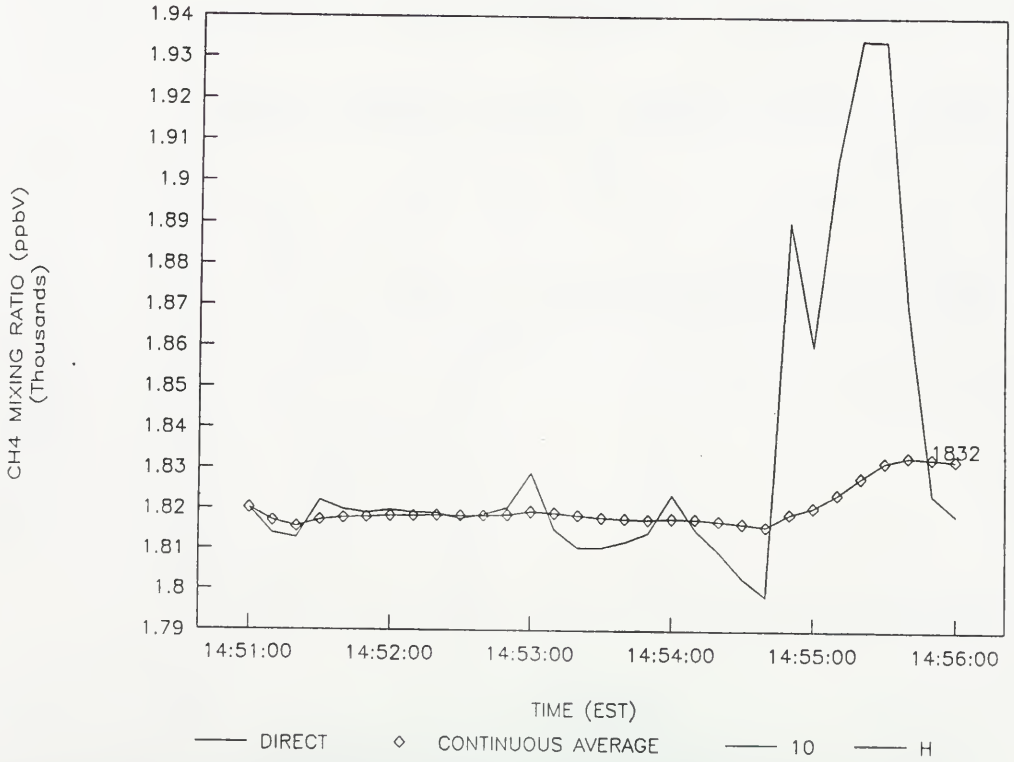
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



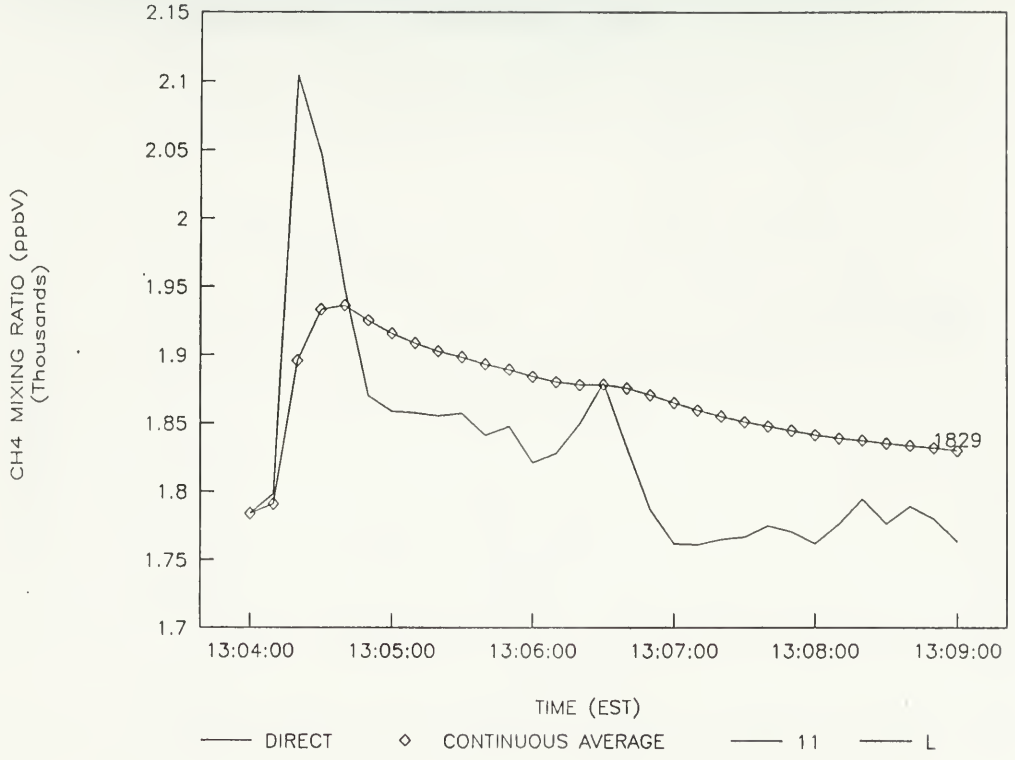
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



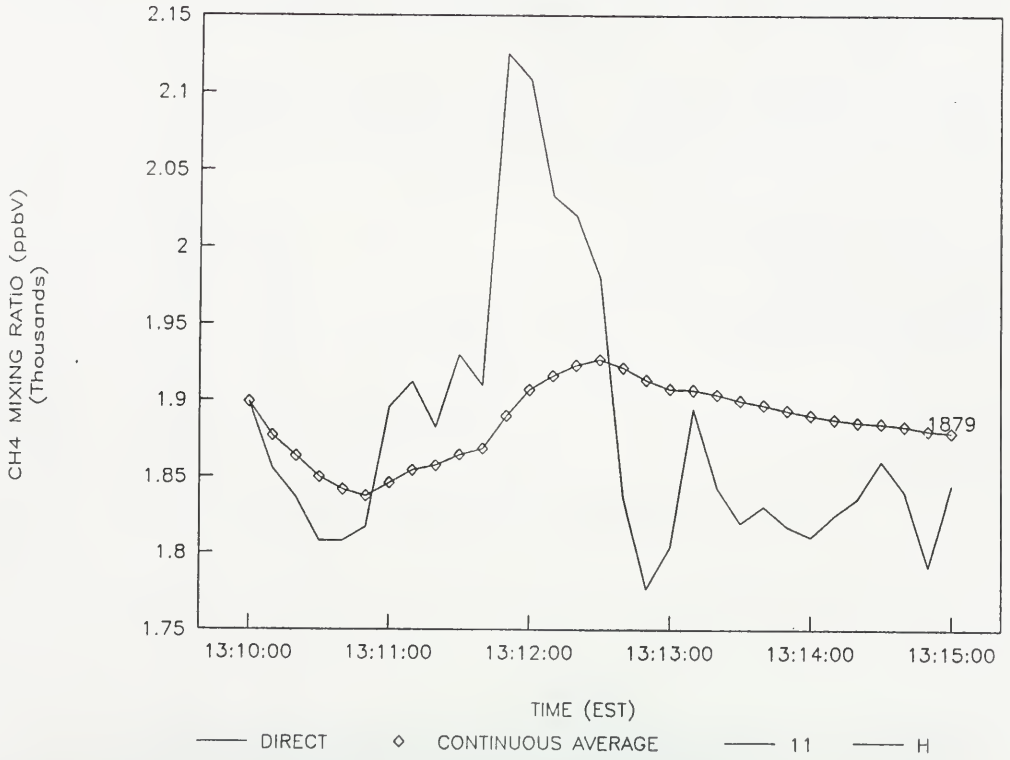
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



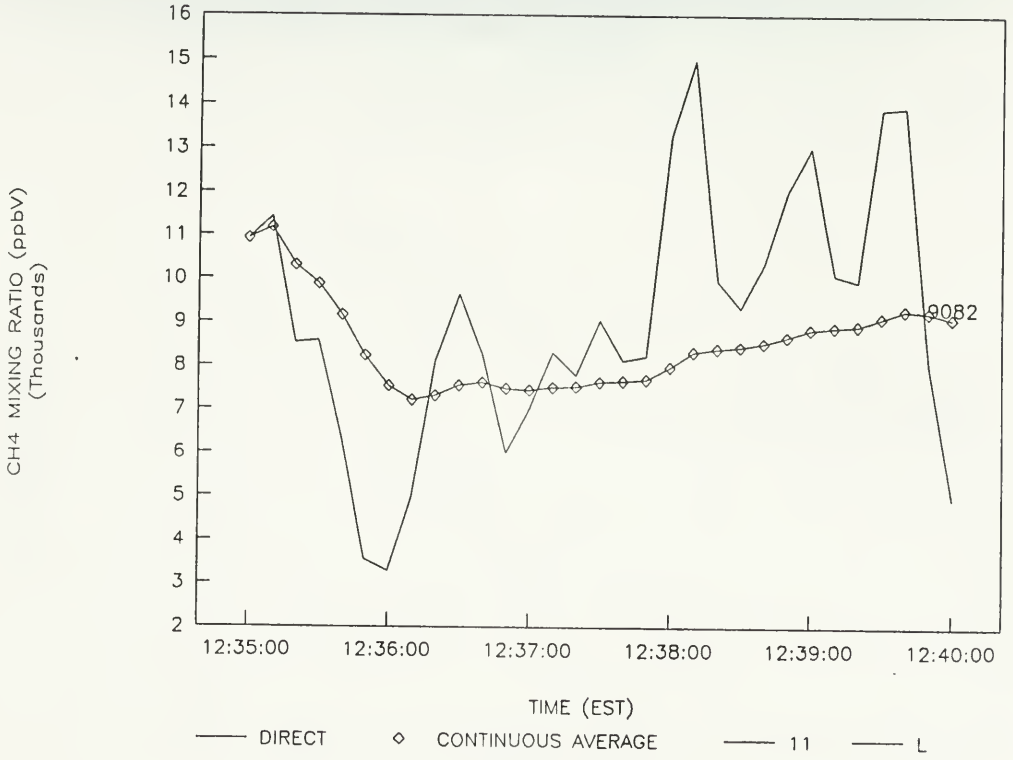
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



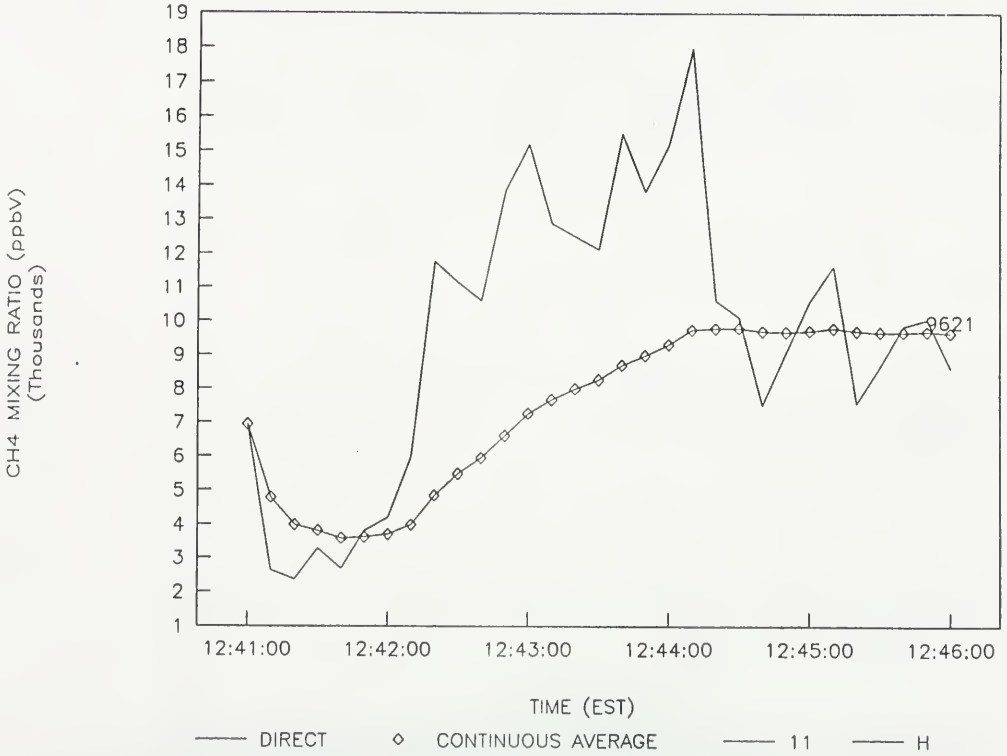
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



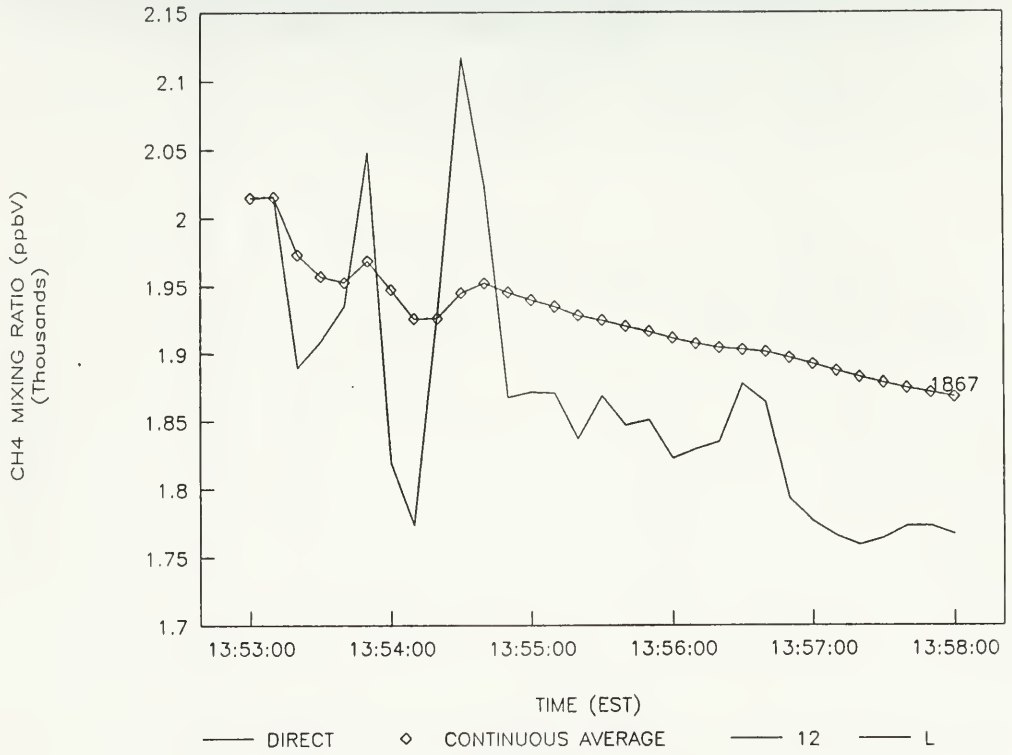
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



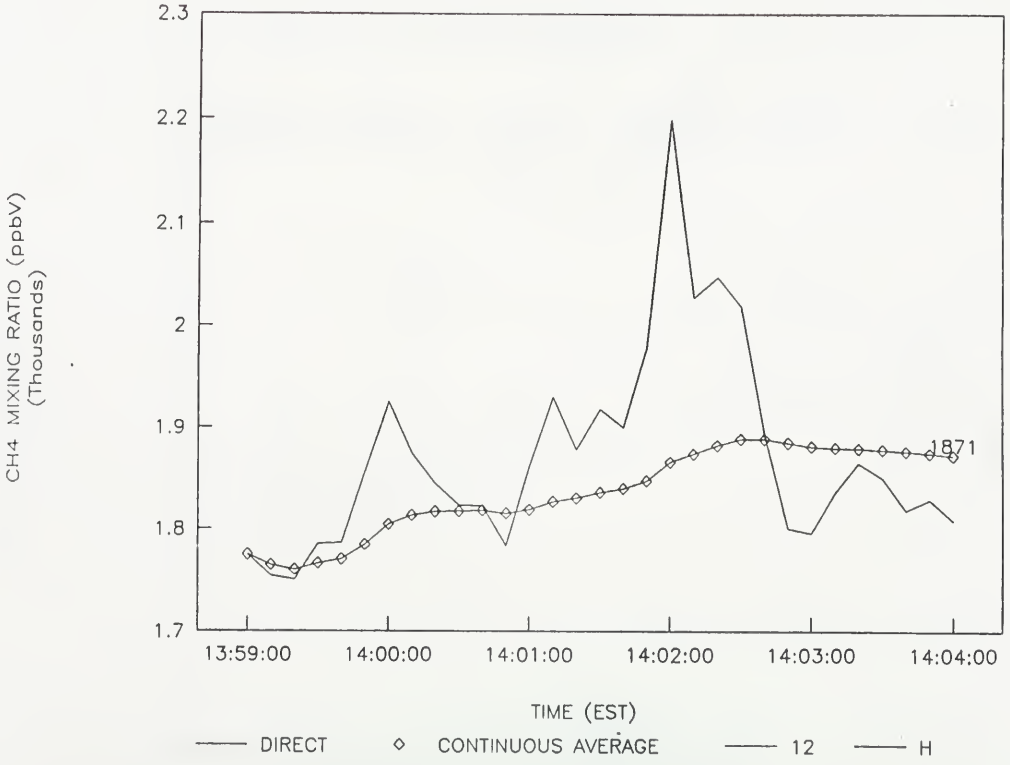
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



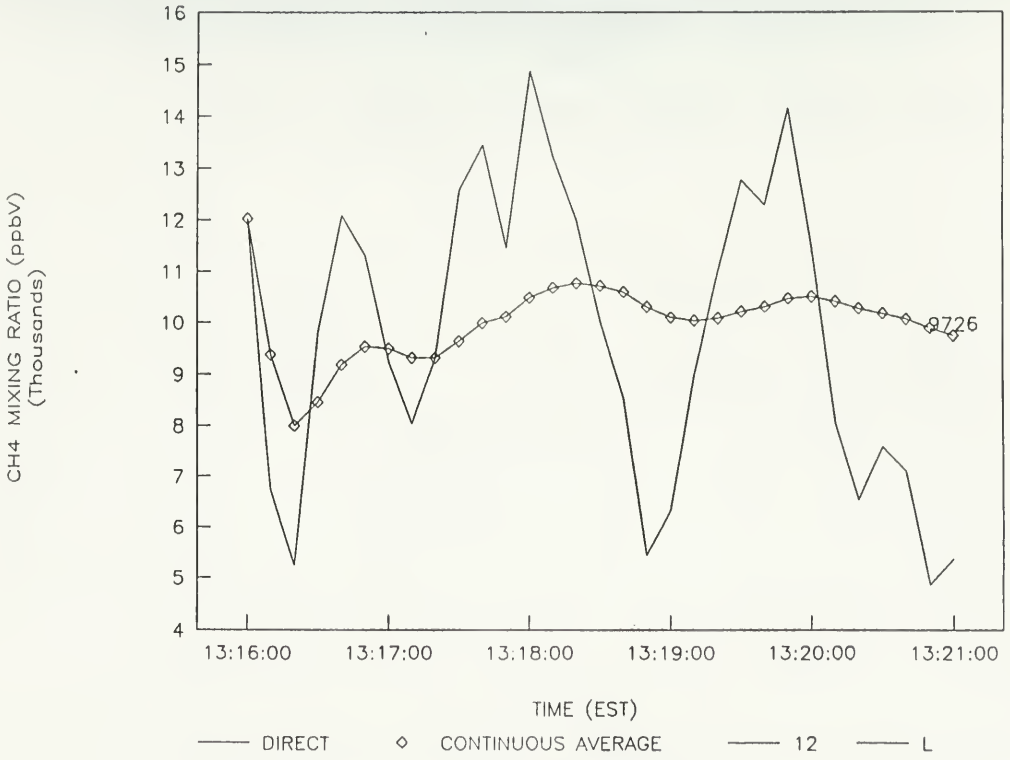
# KEELE VALLEY LANDFILL CH4 STUDY

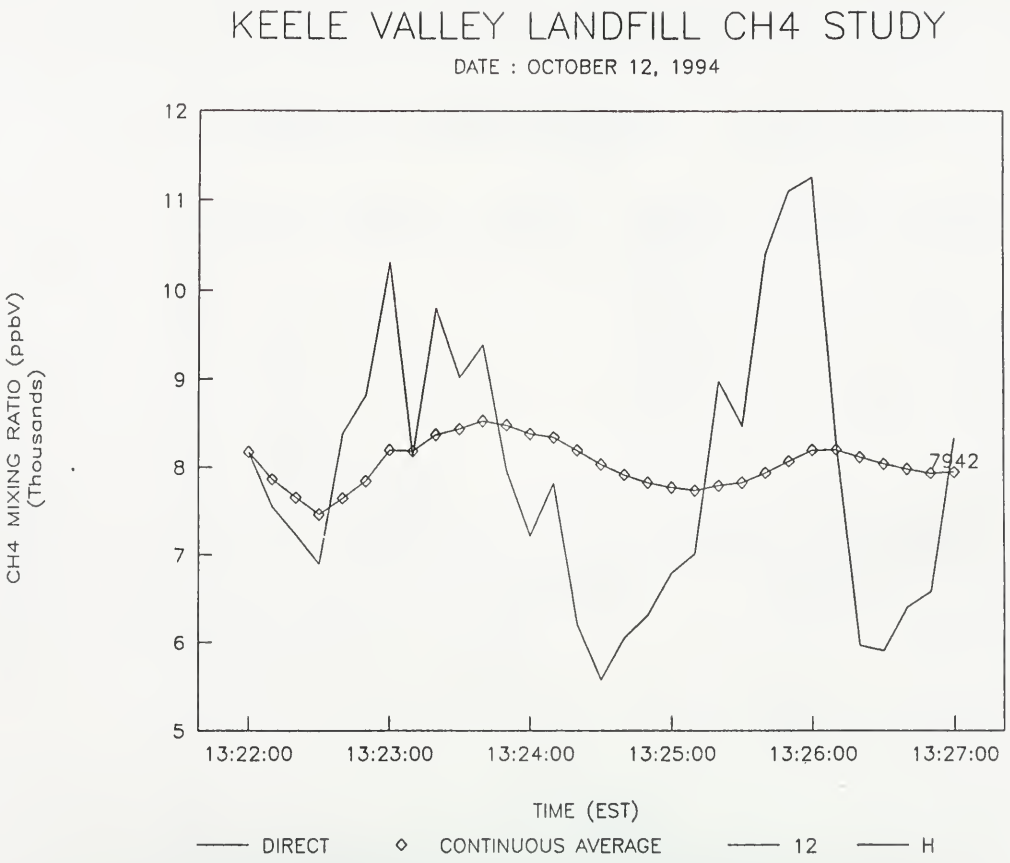
DATE : OCTOBER 6, 1994



# KEELE VALLEY LANDFILL CH4 STUDY

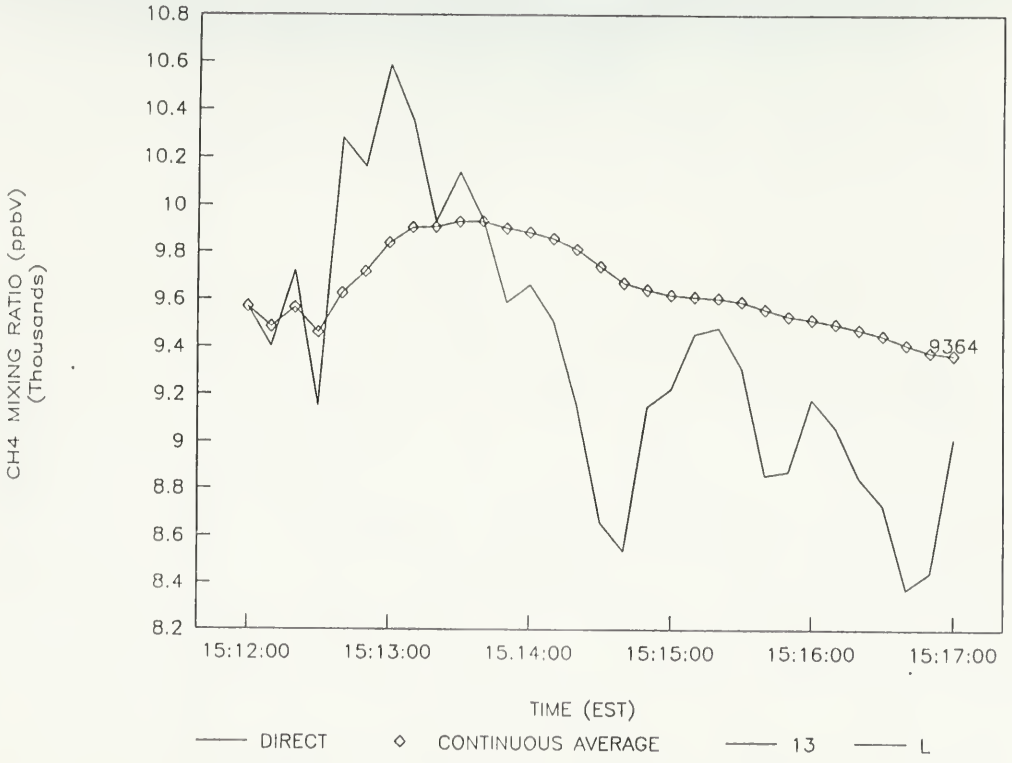
DATE : OCTOBER 12, 1994




KEELE VALLEY LANDFILL CH4 STUDY
DATE : OCTOBER 12, 1994
CH4 MIXING RATIO (ppbV)
(Thousands)
12
11
10
9
8
7
6
5
7942
13:22:00
13:23:00
13:24:00
13:25:00
13:26:00
13:27:00
TIME (EST)
DIRECT
CONTINUOUS AVERAGE
12
H

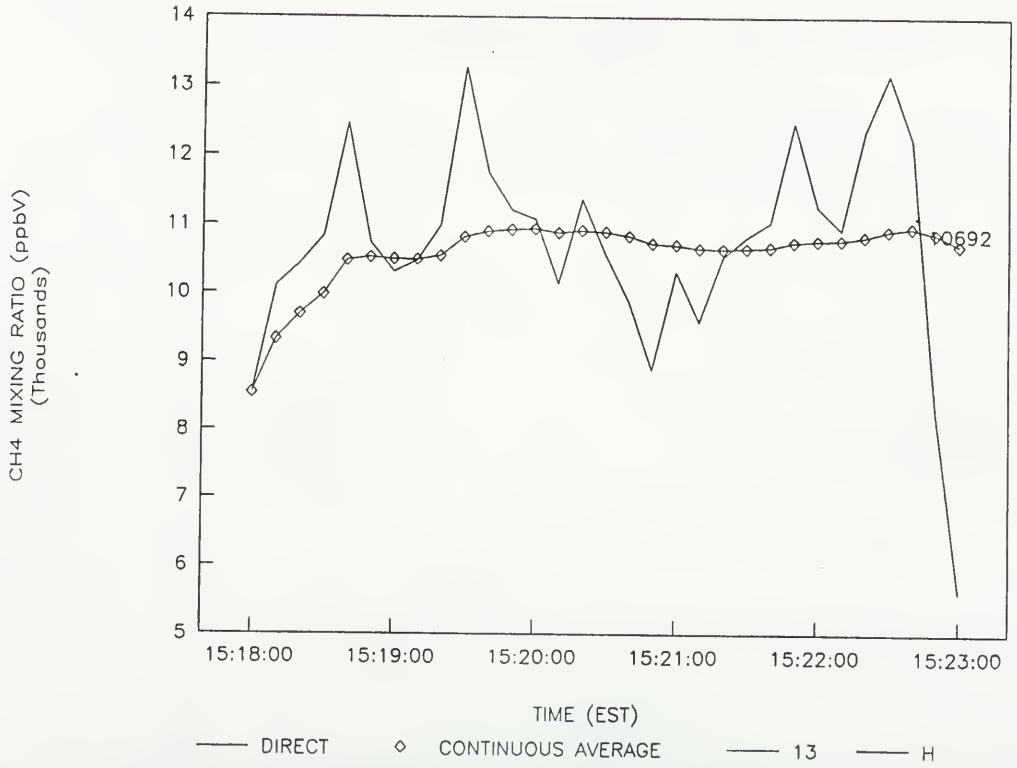
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 23, 1994



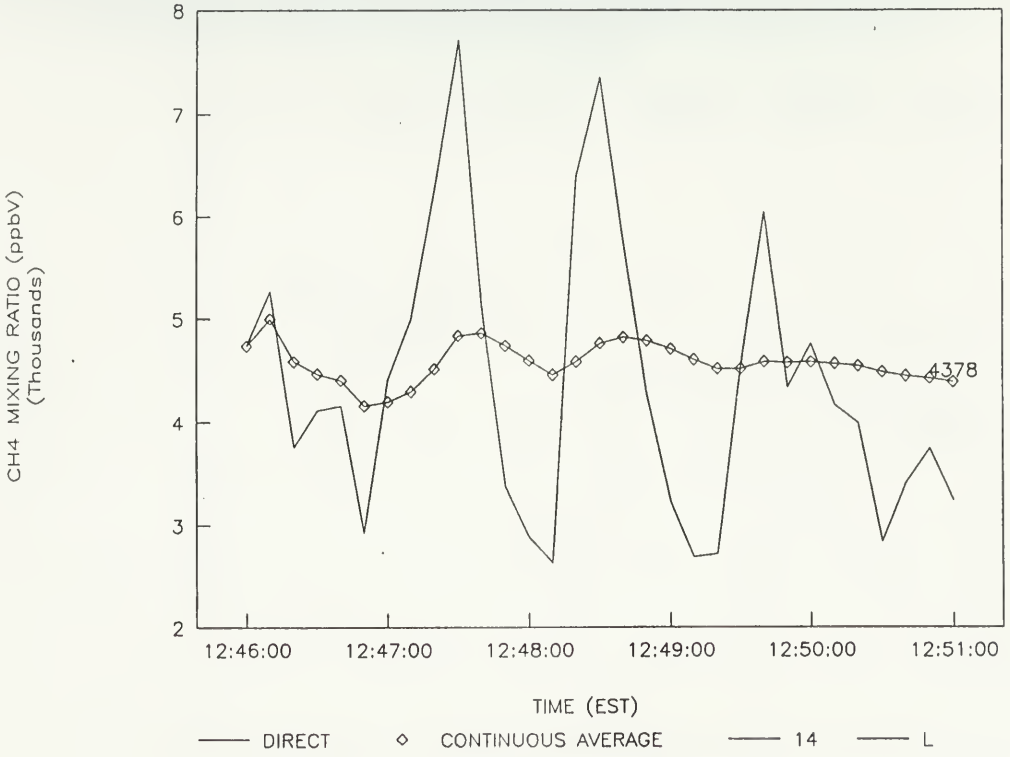
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 23, 1994



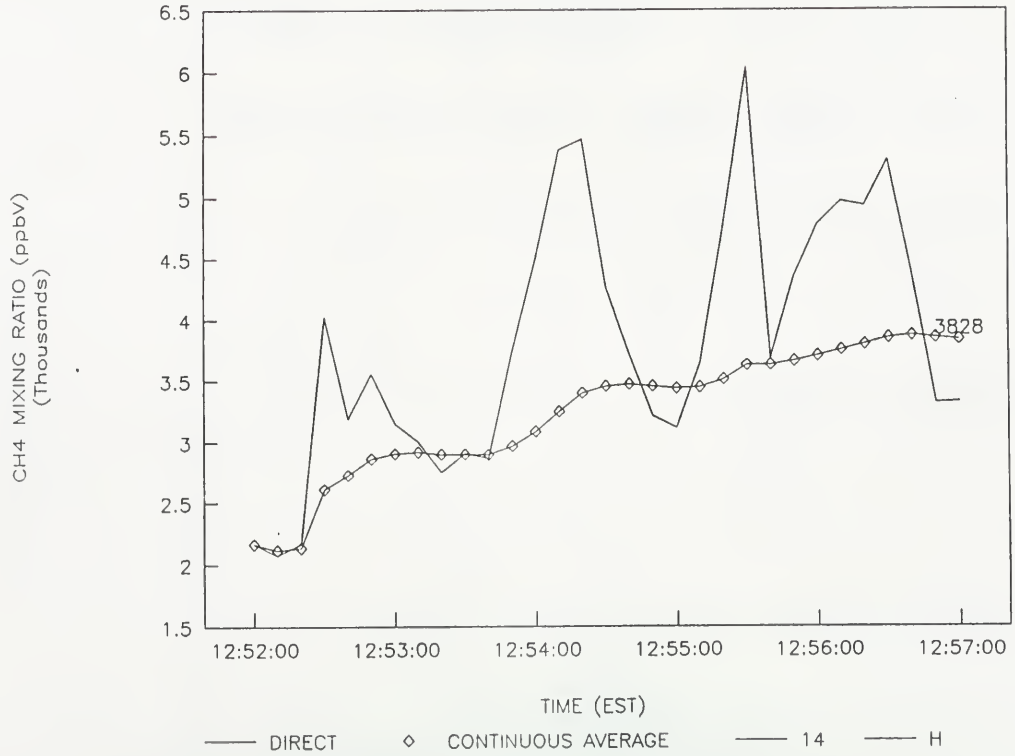
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 7, 1994



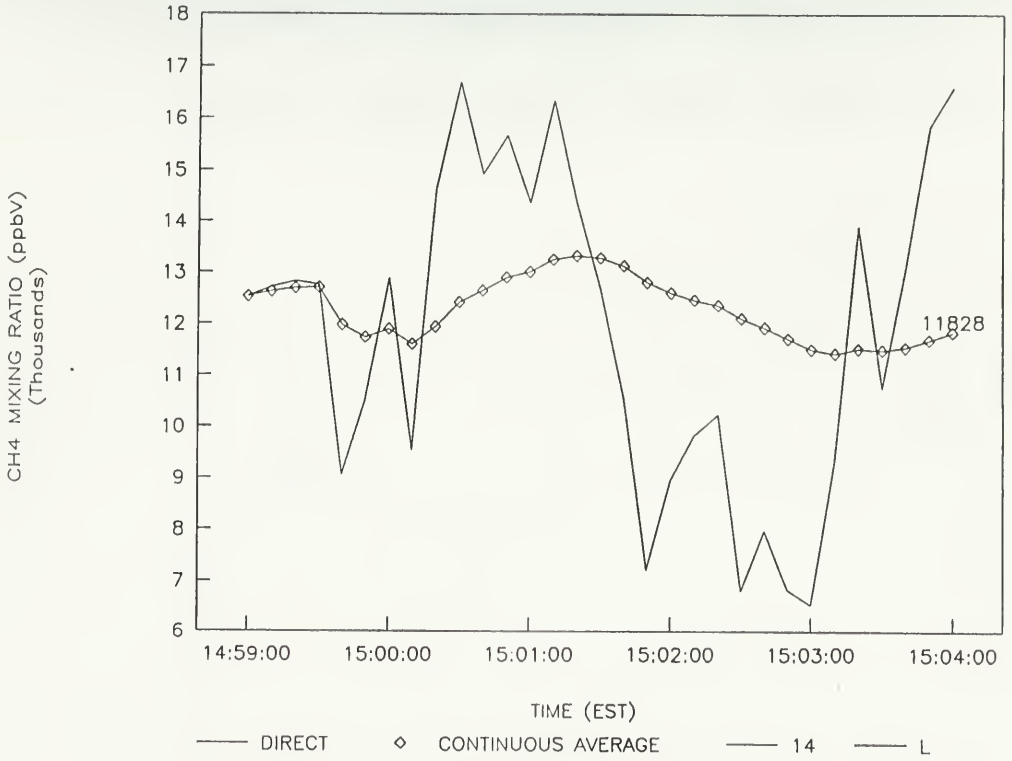
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 7, 1994



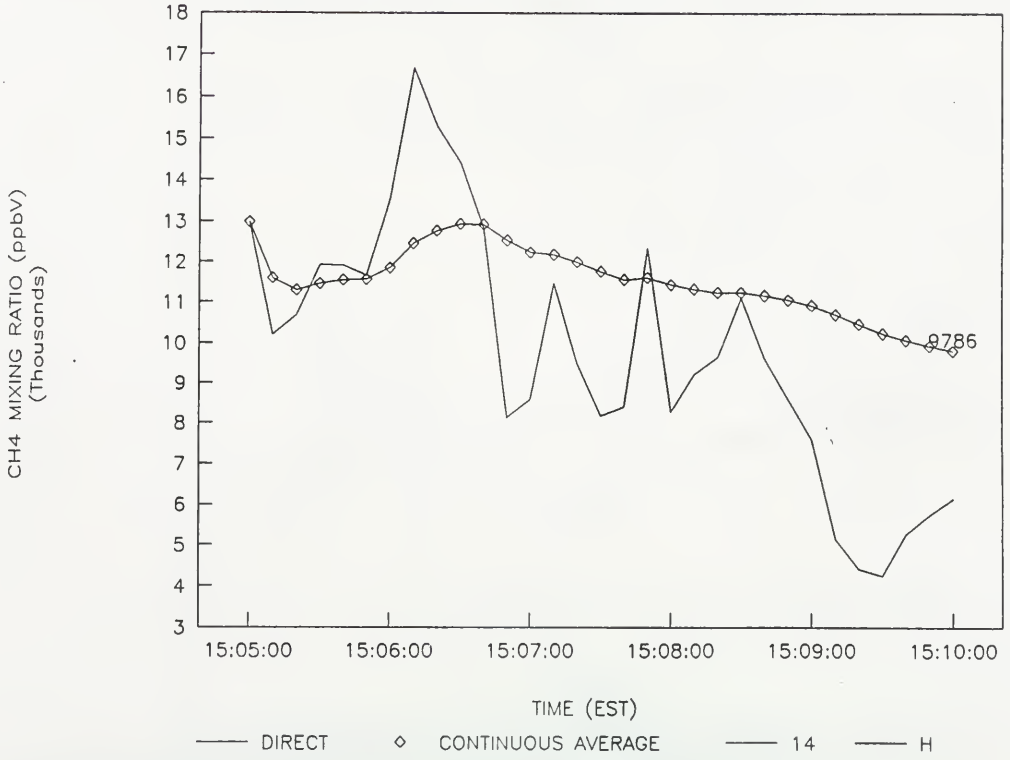
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 23, 1994



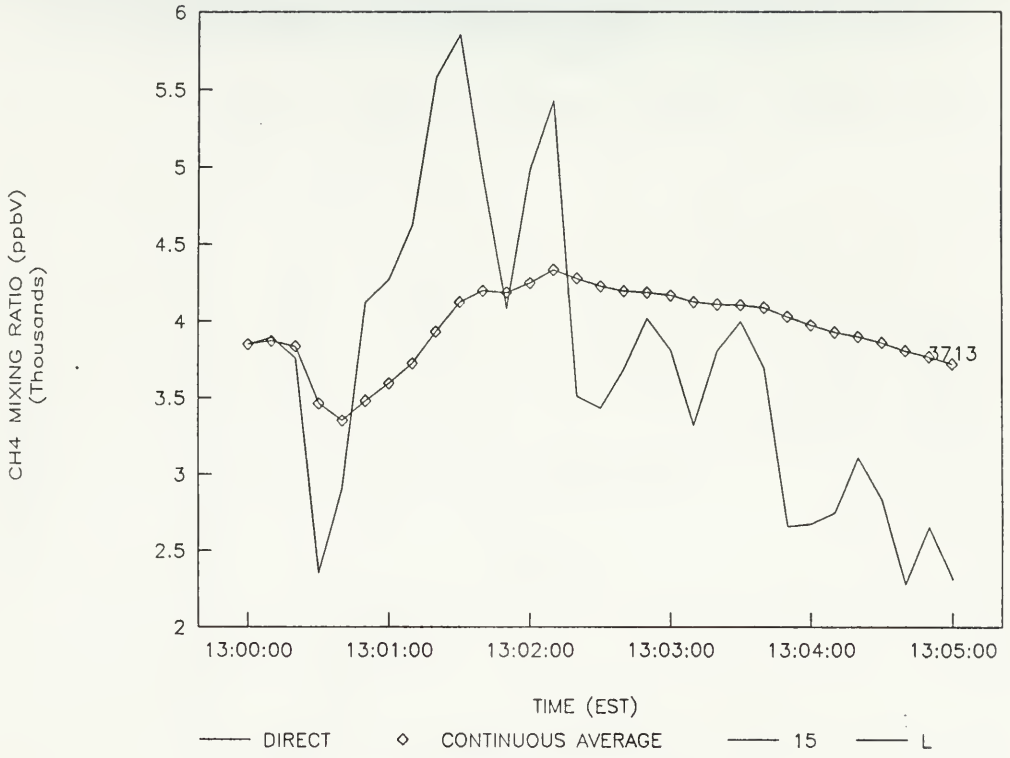
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 23, 1994



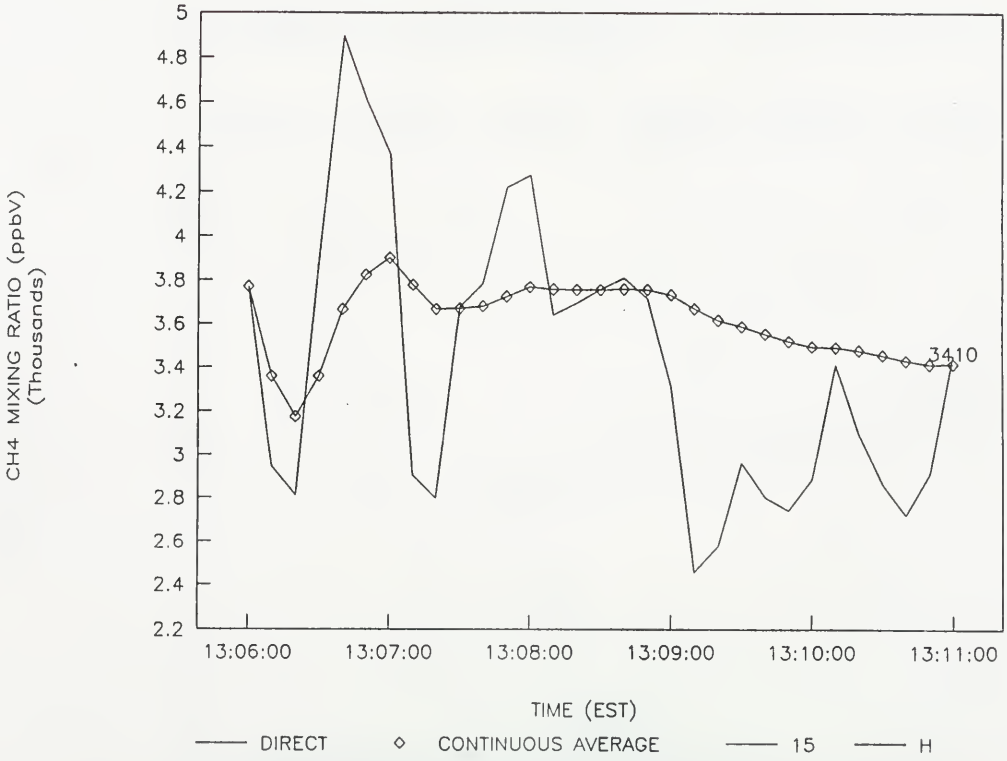
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 7, 1994



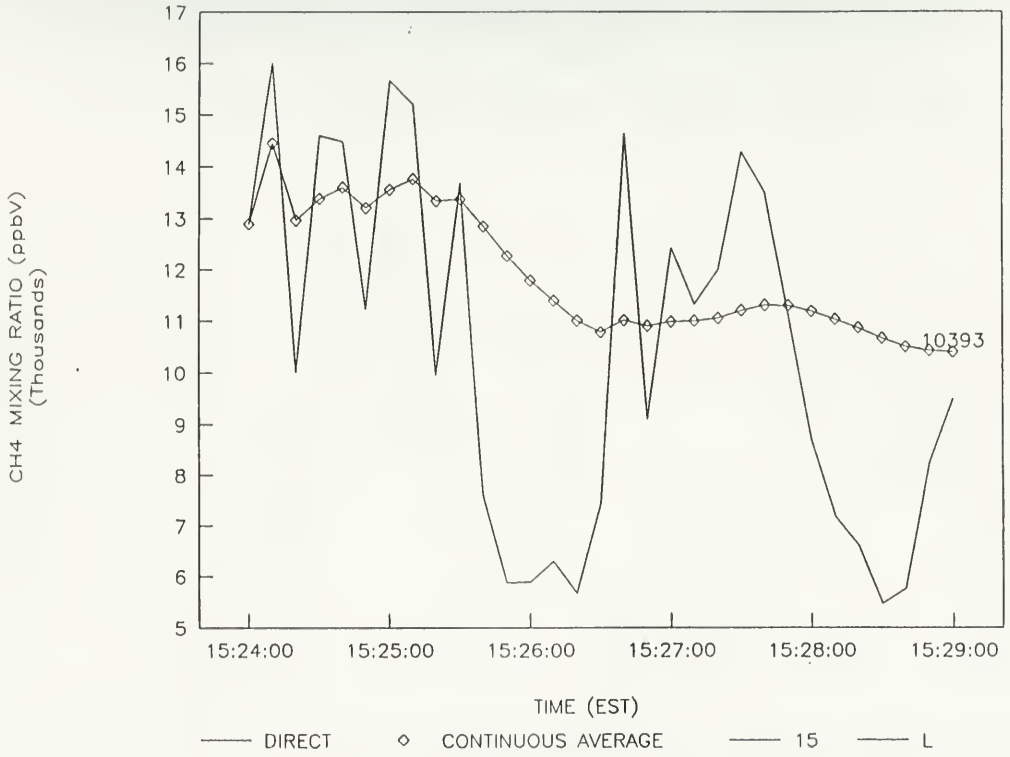
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 7, 1994



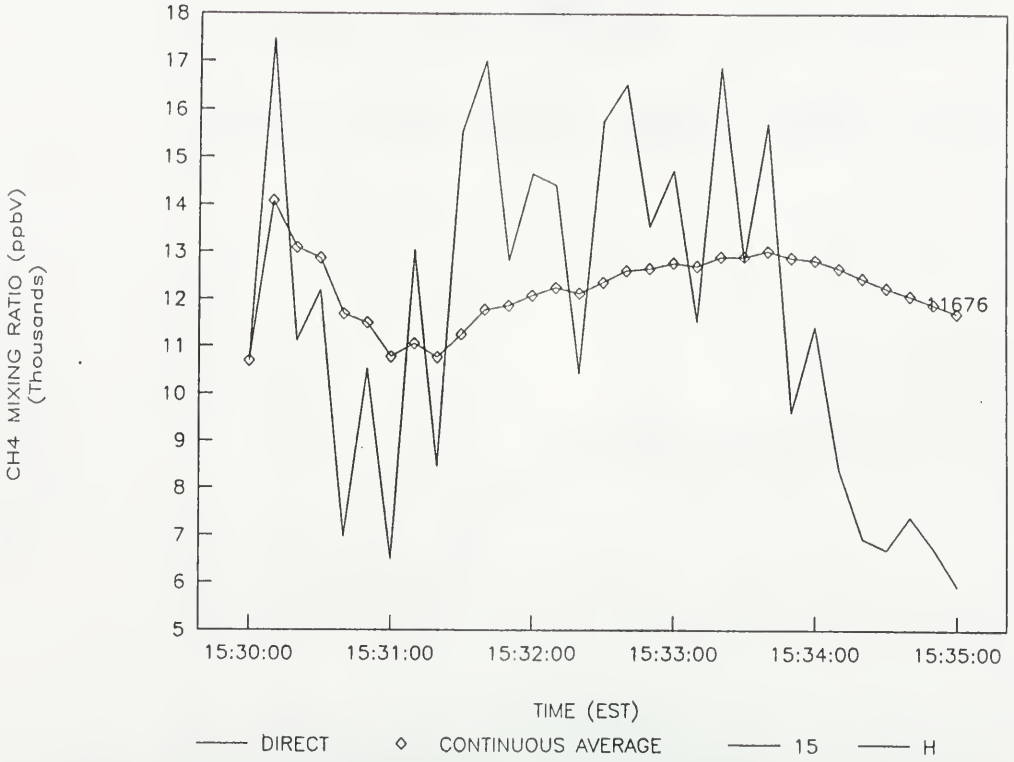
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 23, 1994



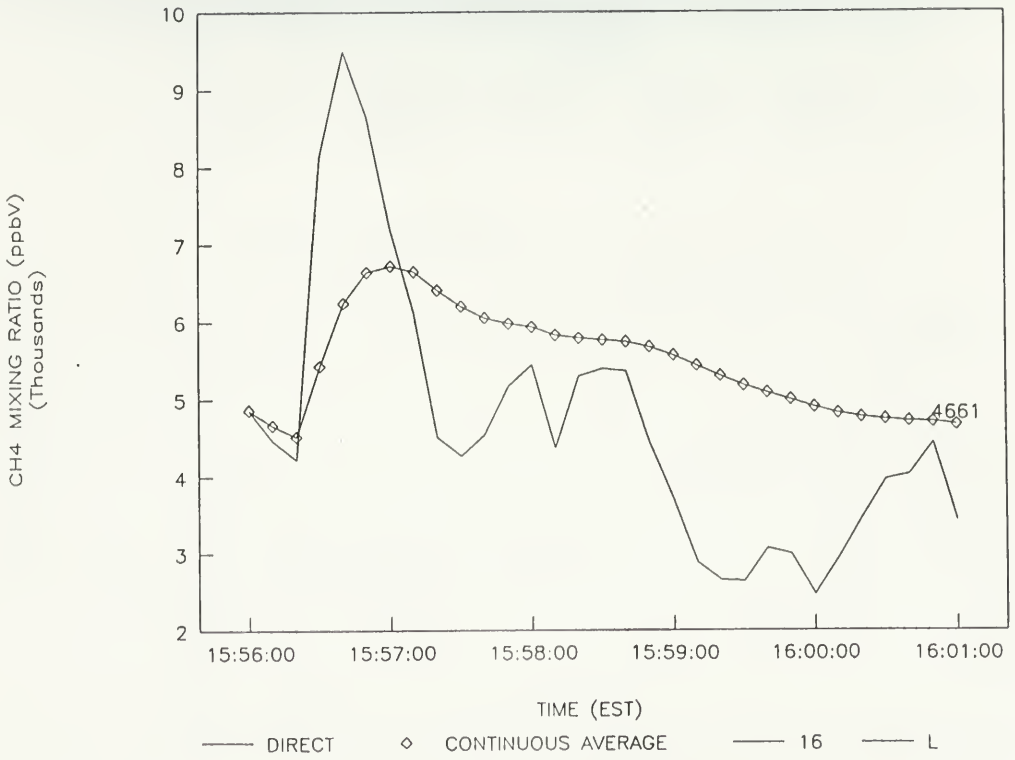
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 23, 1994



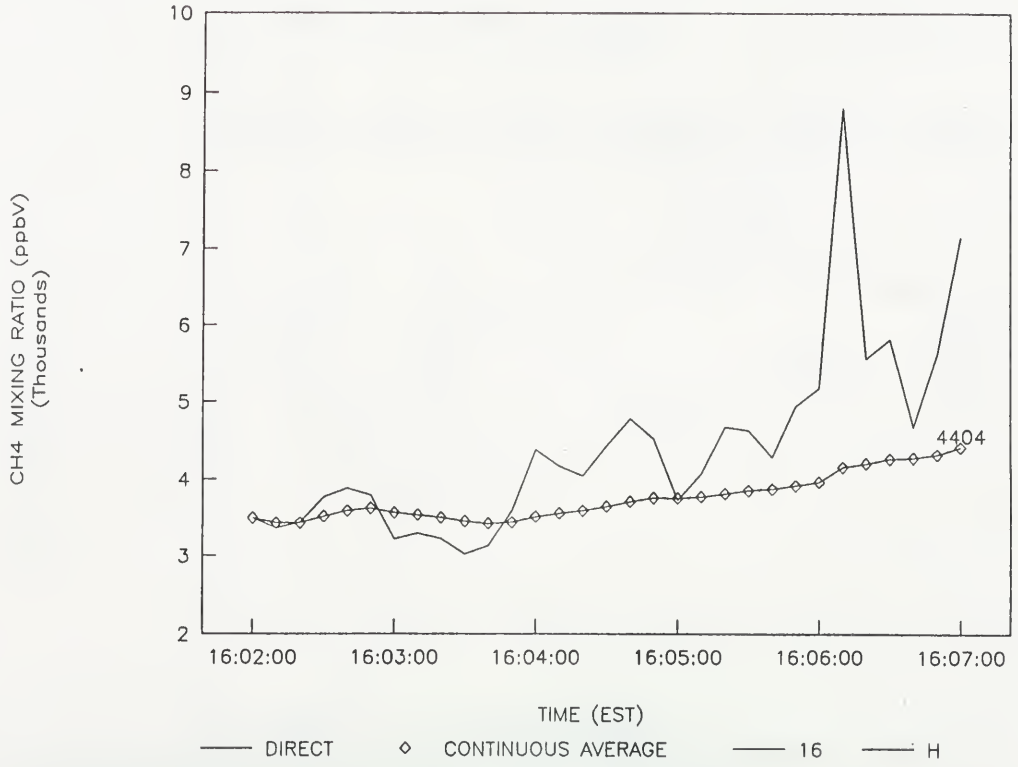
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



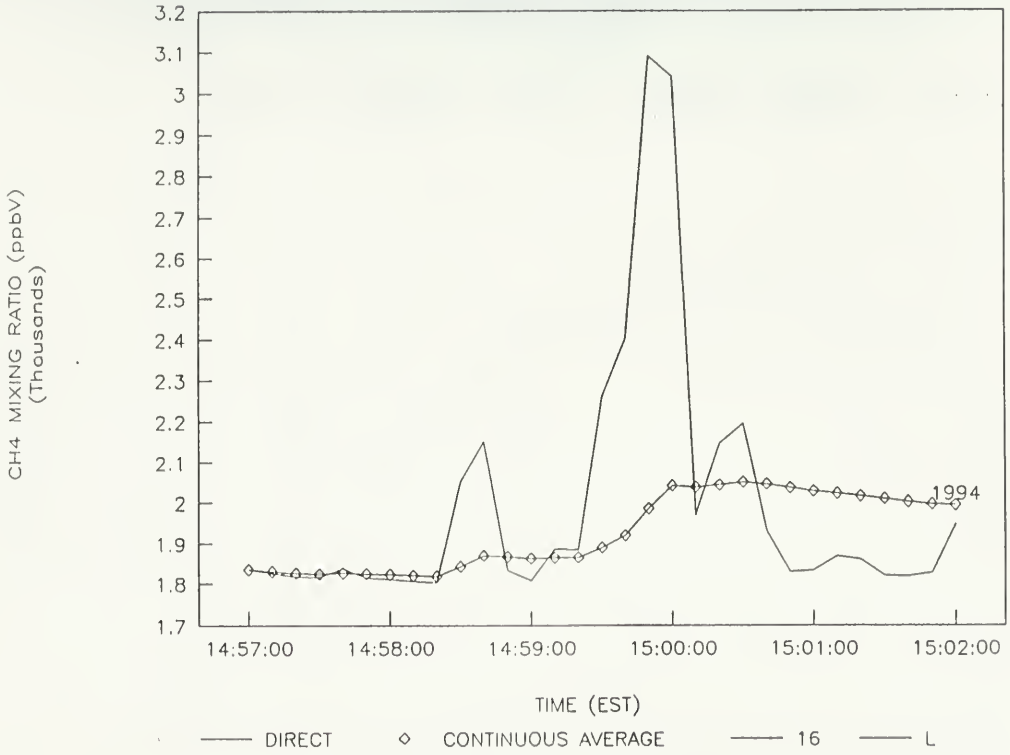
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



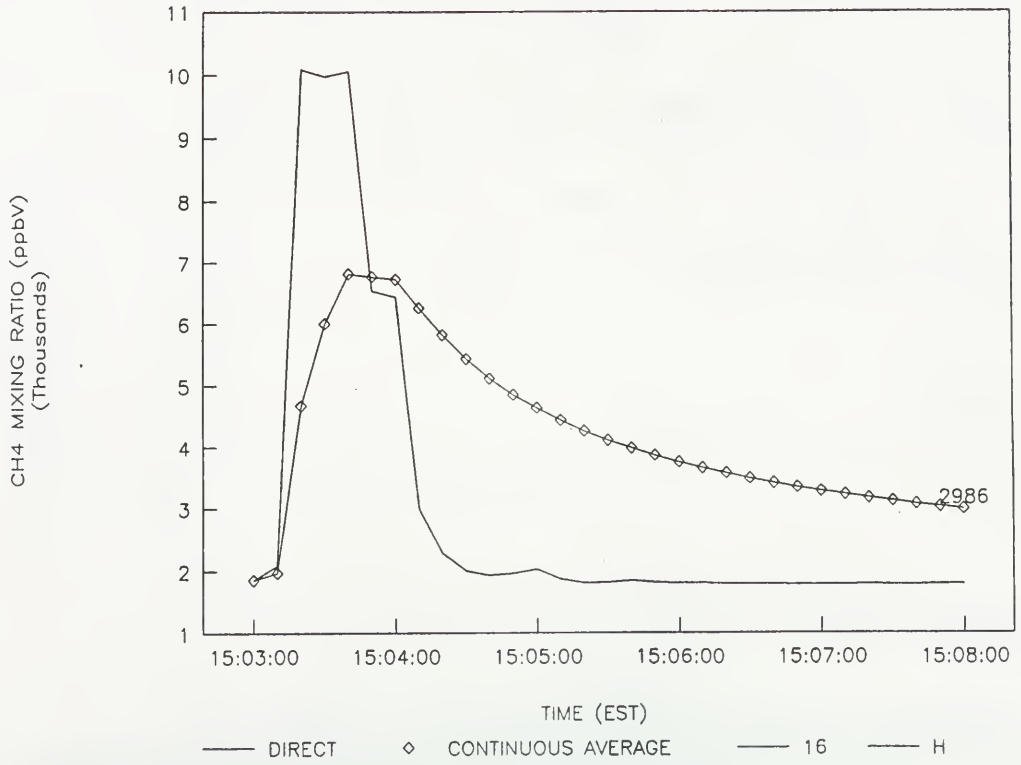
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



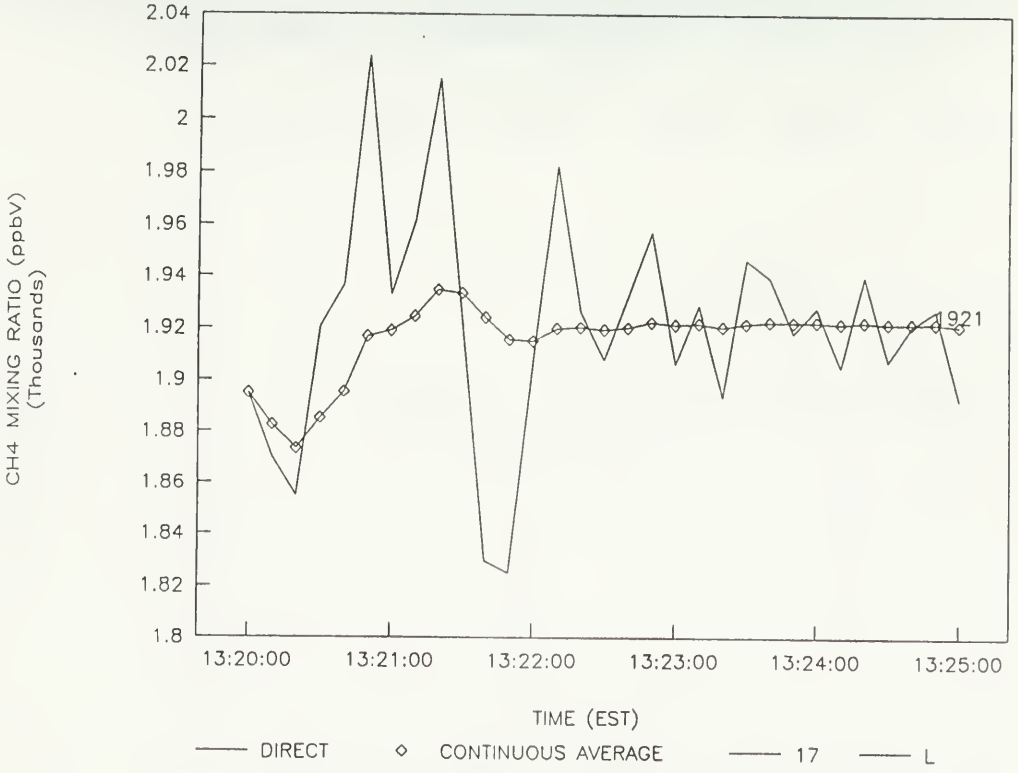
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



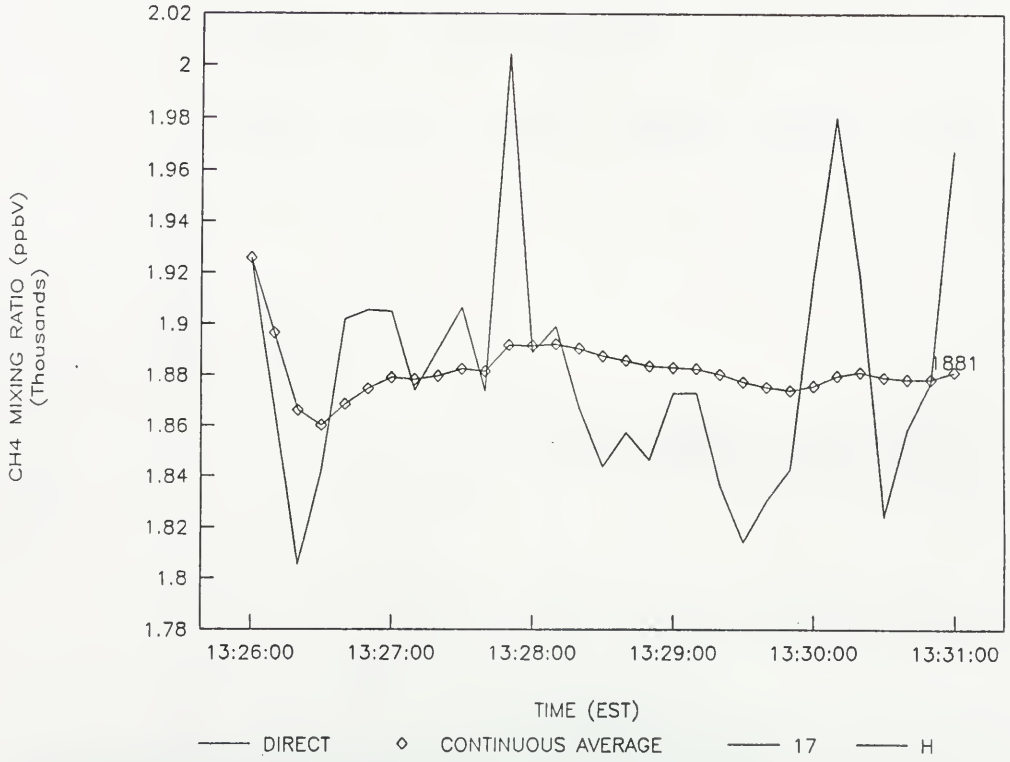
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



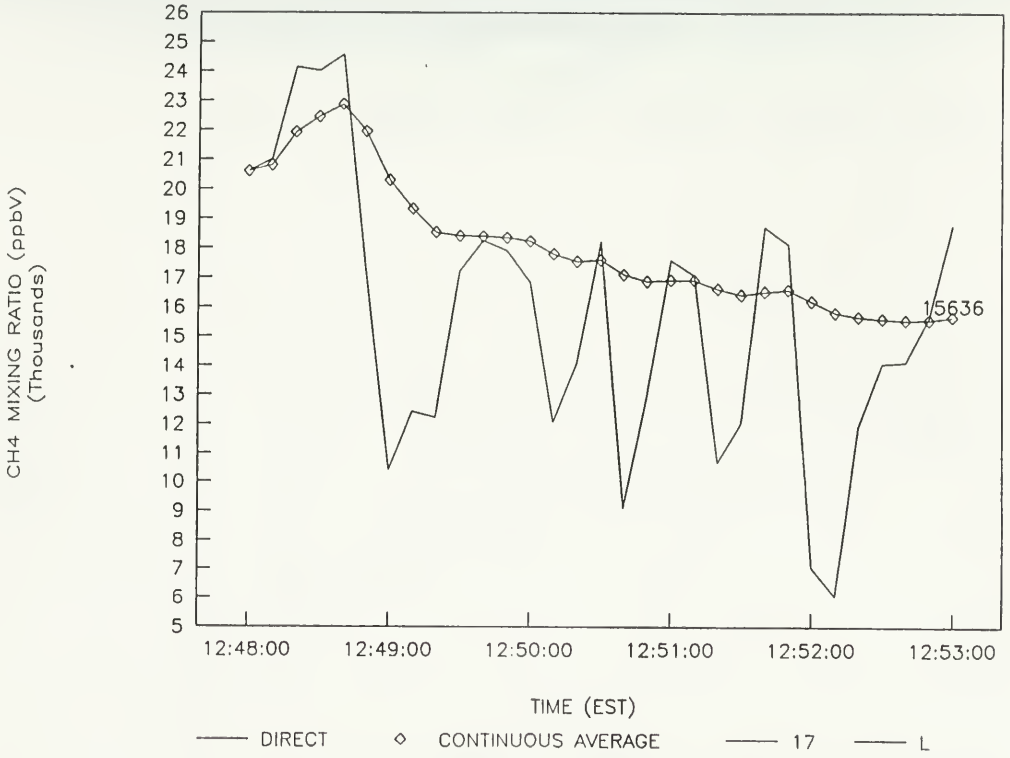
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



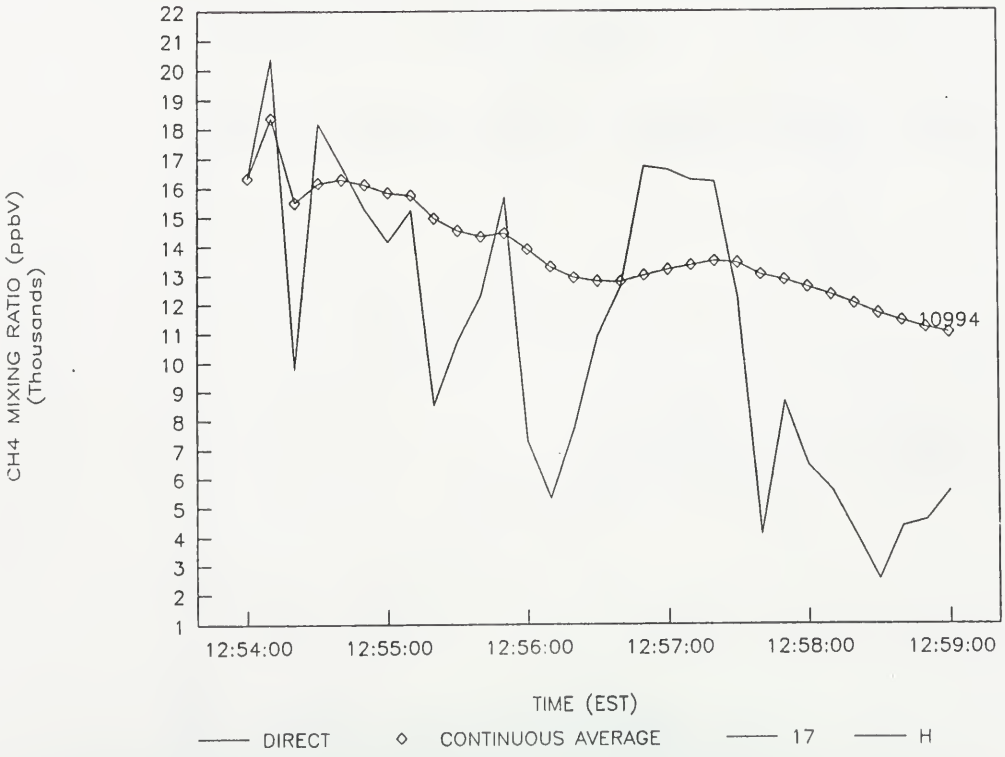
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



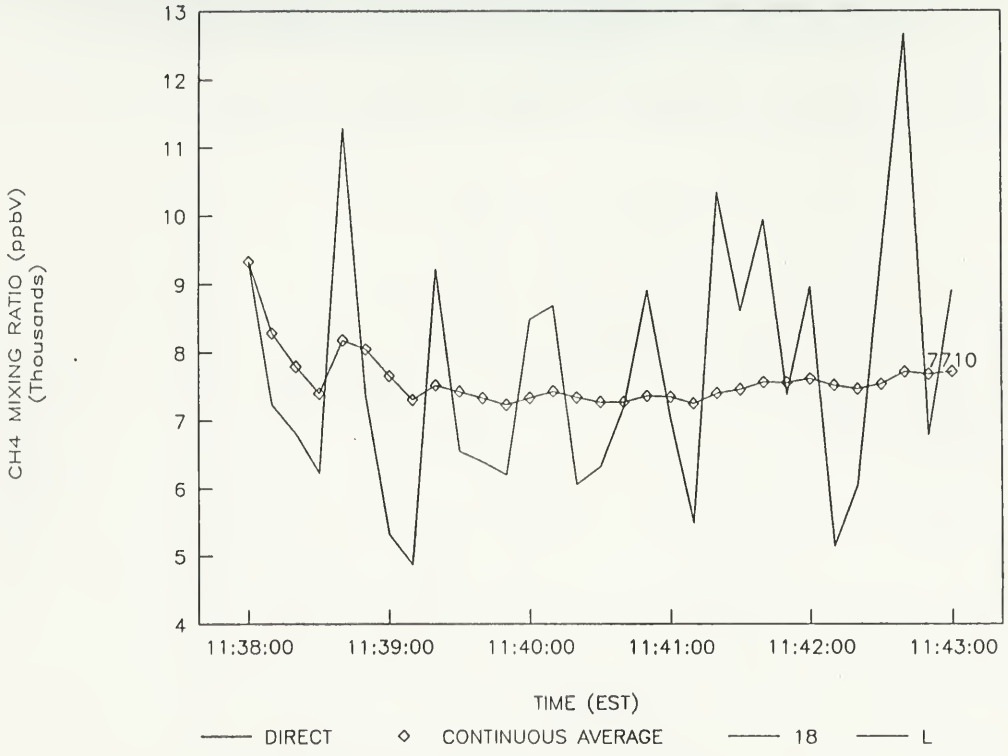
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



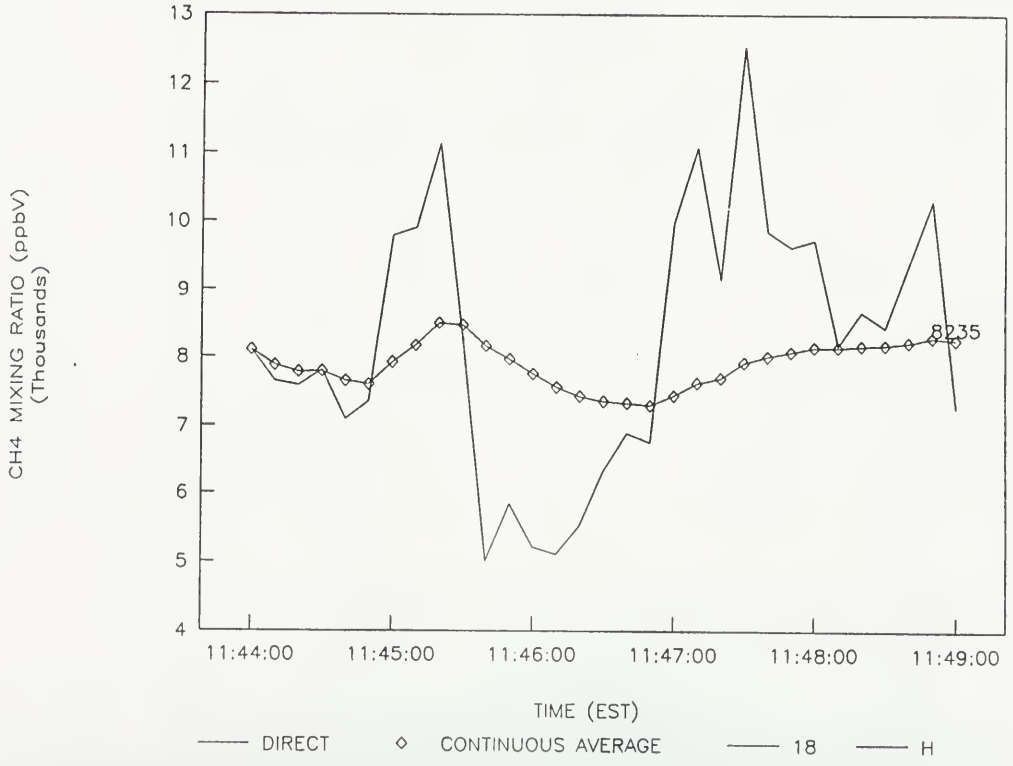
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 7, 1994



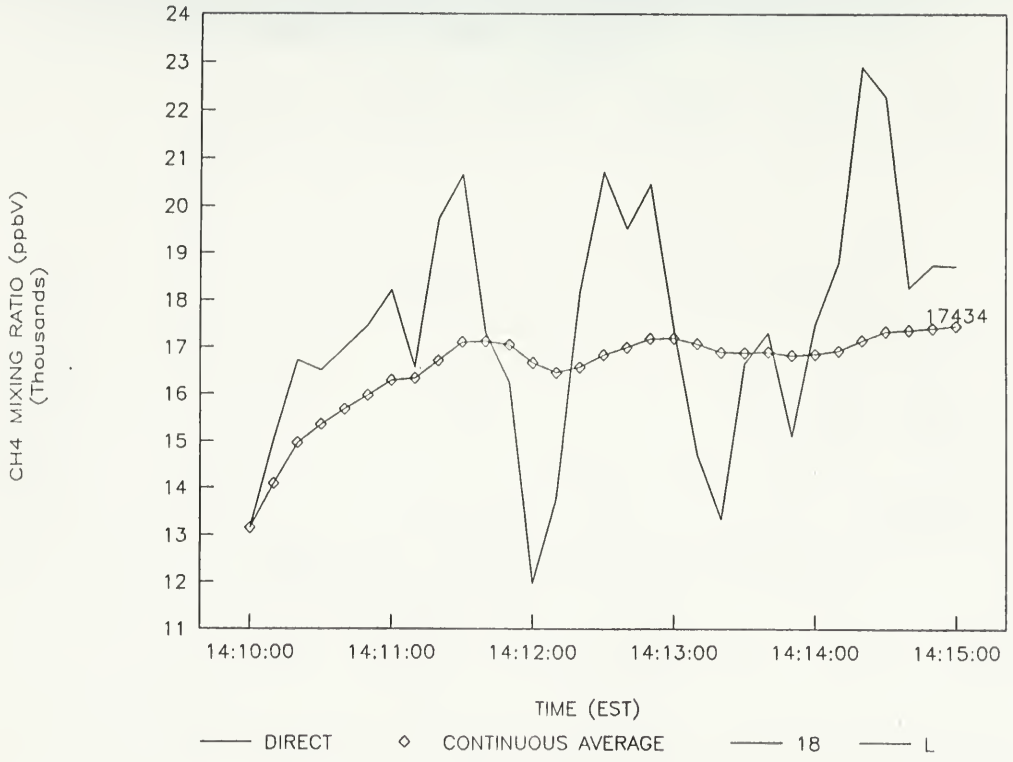
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 7, 1994



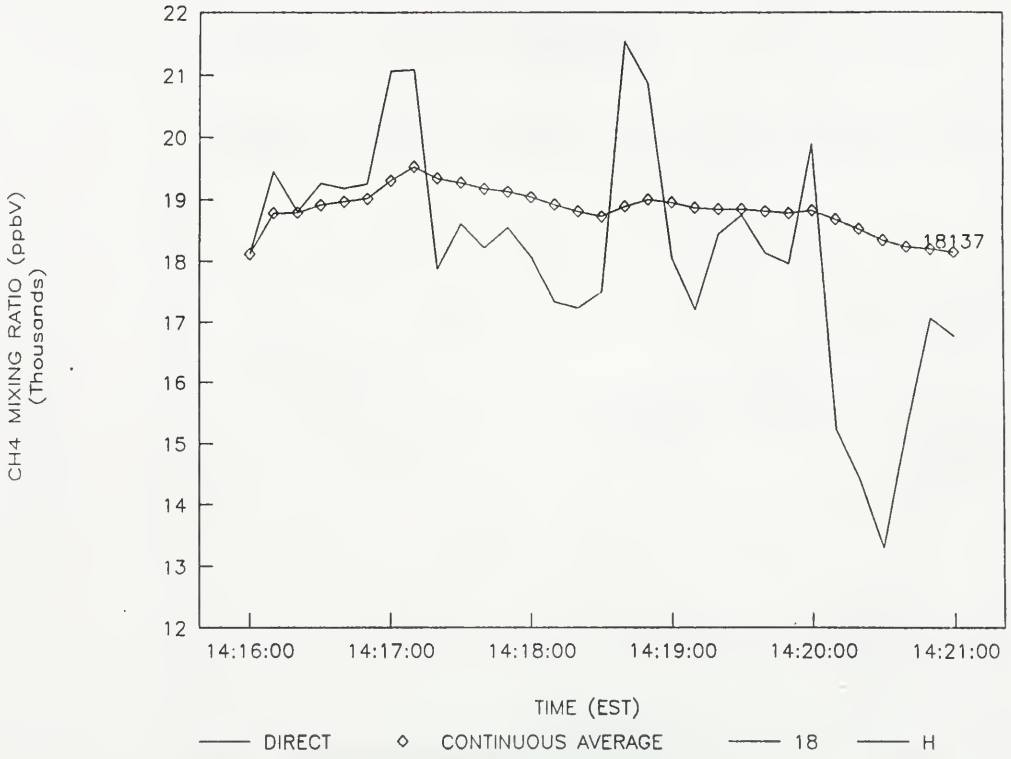
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 23, 1994



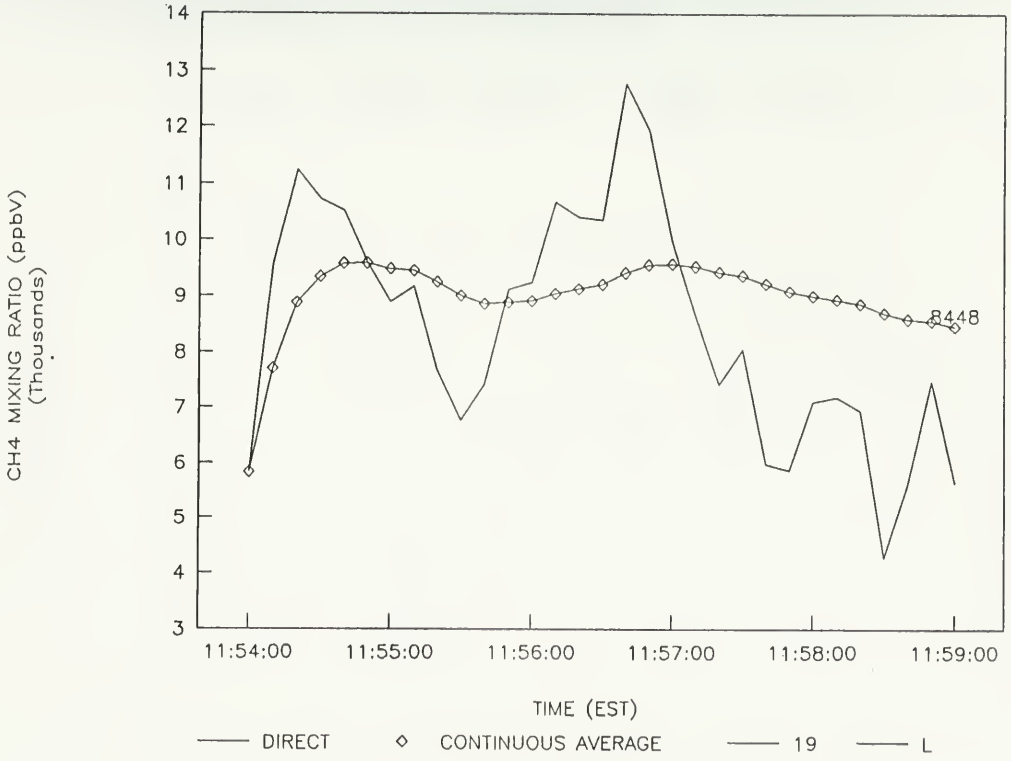
# KEELE VALLEY LANDFILL CH4 STUDY

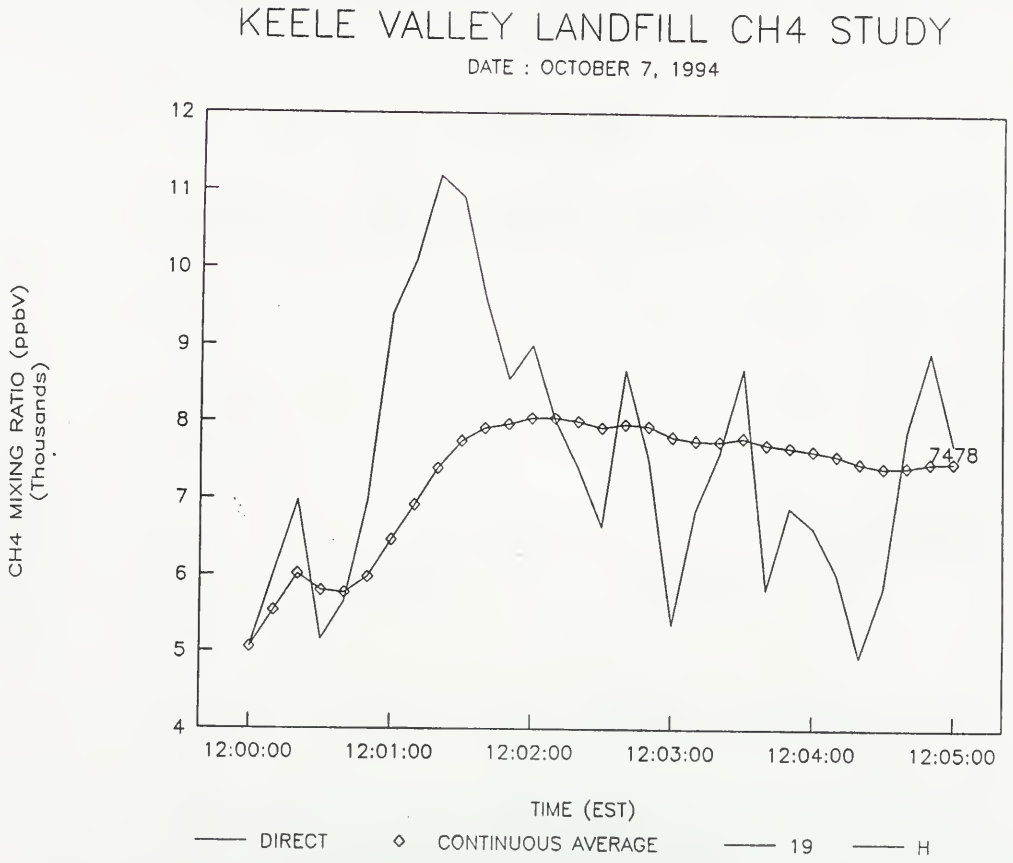
DATE : OCTOBER 23, 1994



# KEELE VALLEY LANDFILL CH4 STUDY

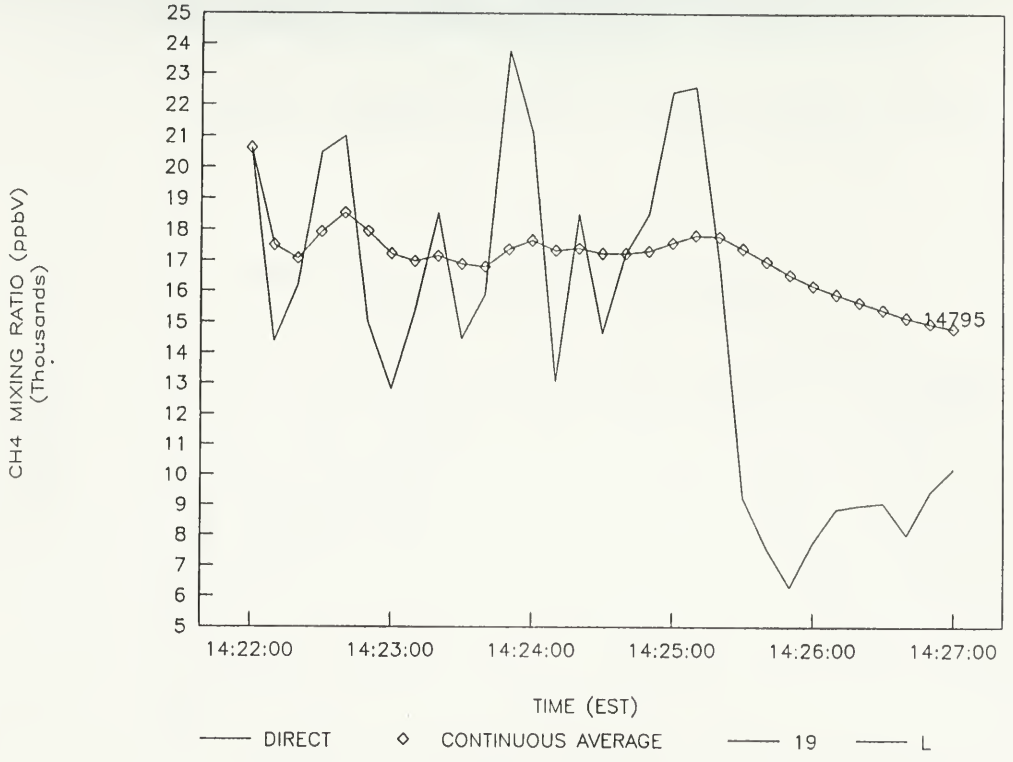
DATE : OCTOBER 7, 1994




KEELE VALLEY LANDFILL CH4 STUDY
DATE : OCTOBER 7, 1994
CH4 MIXING RATIO (ppbV)
(Thousands)
12
11
10
9
8
7
6
5
4
7478
12:00:00
12:01:00
12:02:00
12:03:00
12:04:00
12:05:00
TIME (EST)
DIRECT
CONTINUOUS AVERAGE
19
H

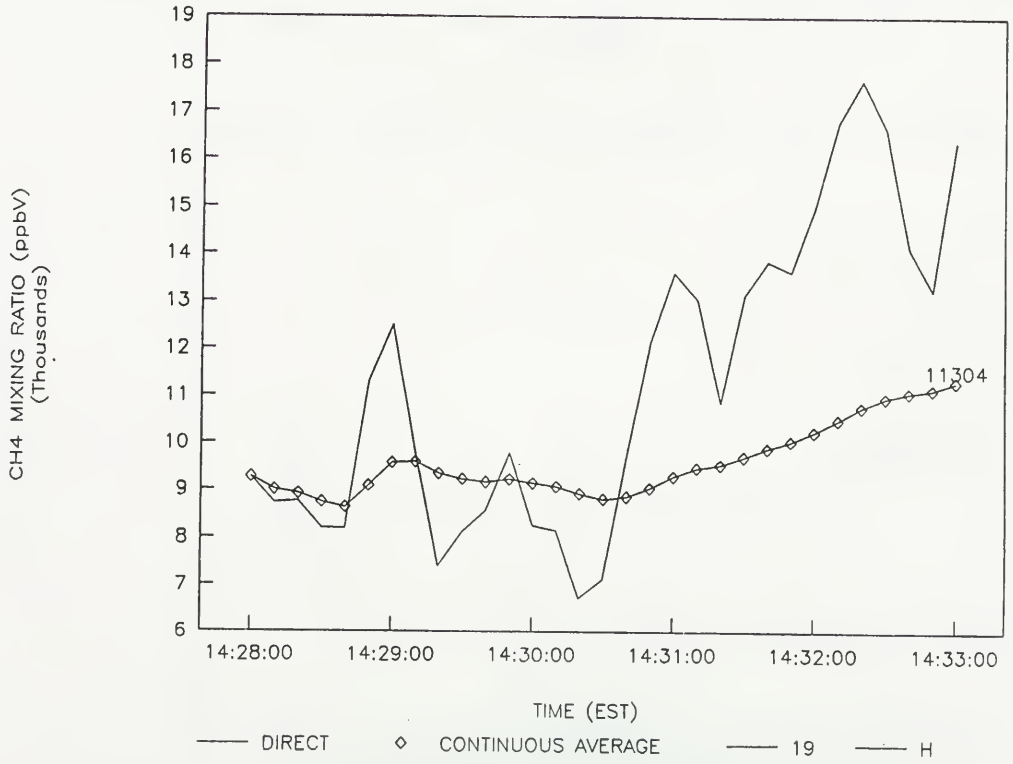
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 23, 1994



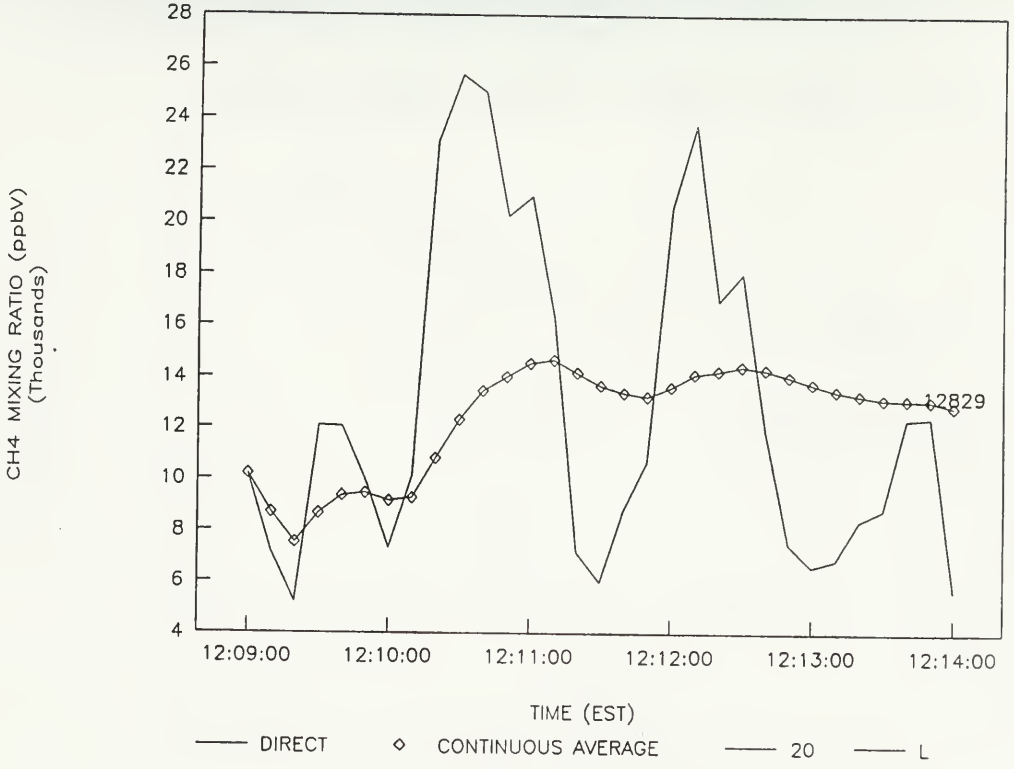
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 23, 1994



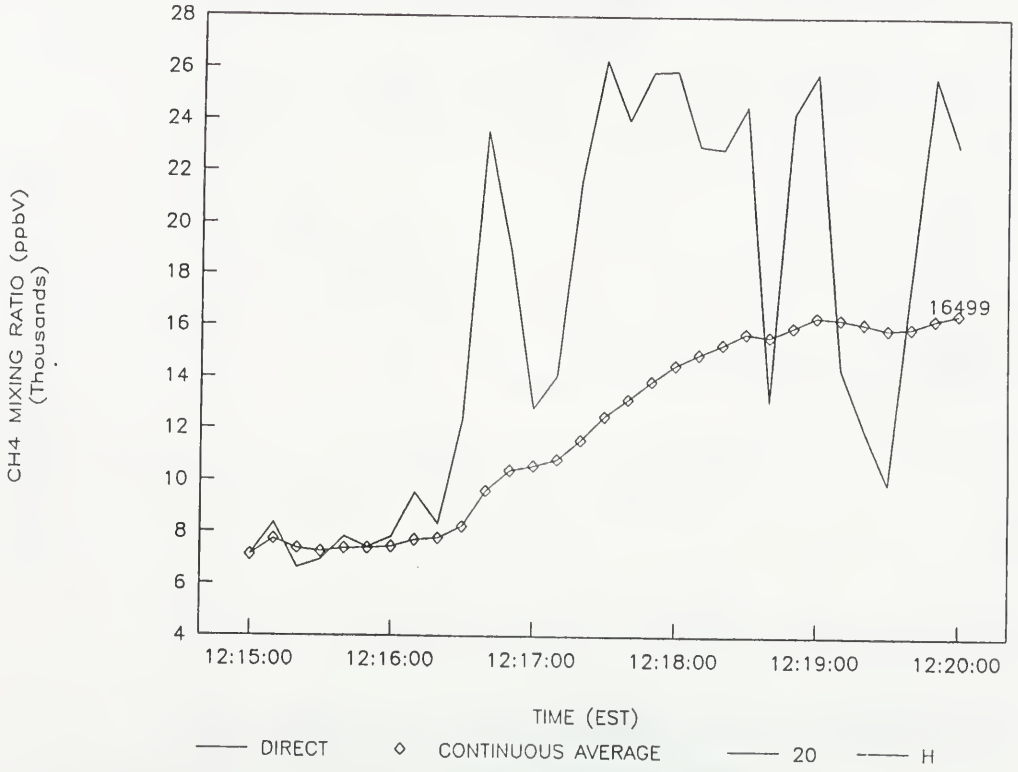
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 7, 1994



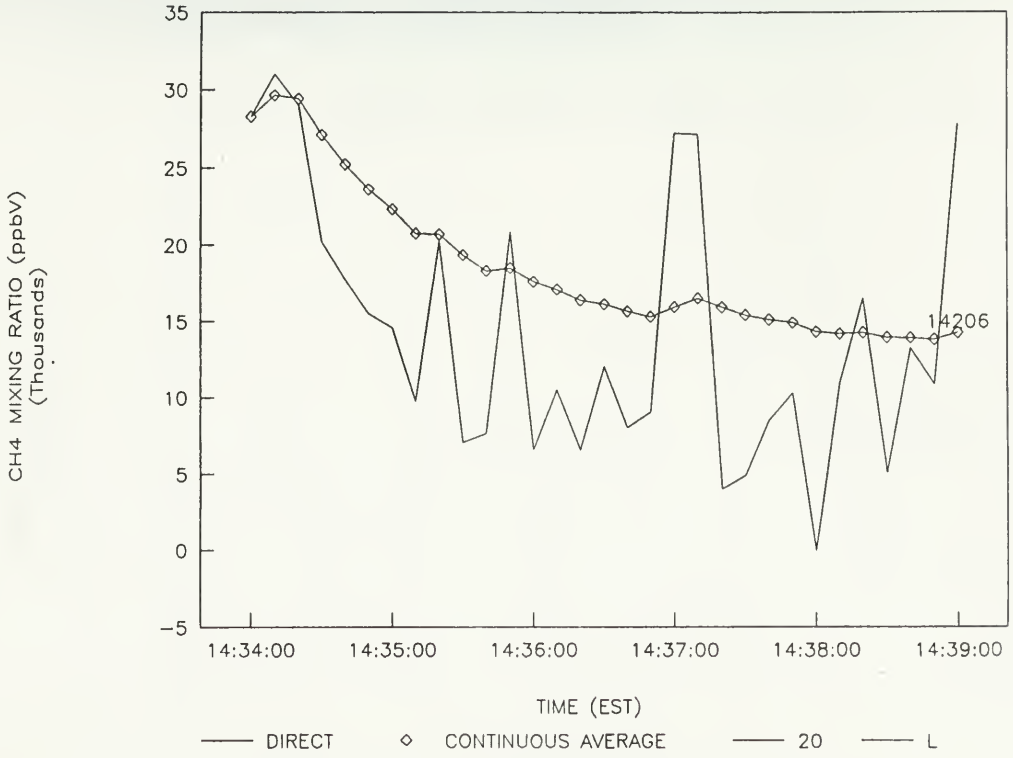
# KEELE VALLEY LANDFILL CH4 STUDY

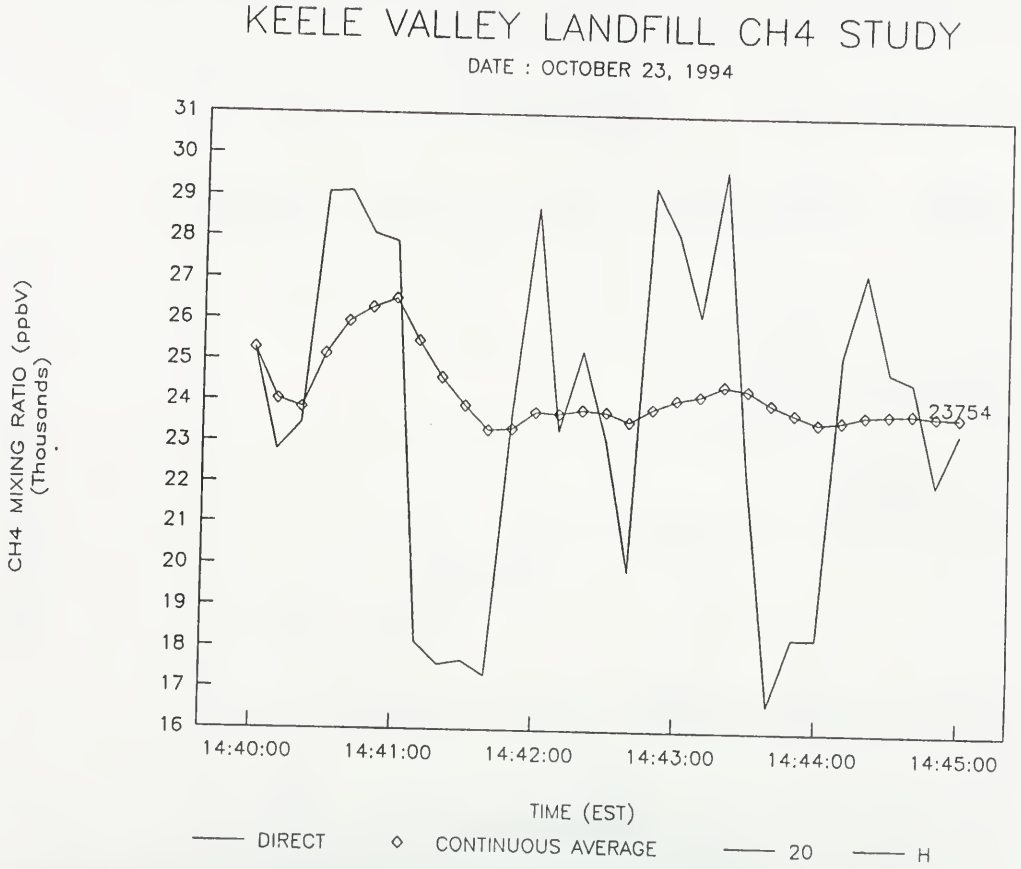
DATE : OCTOBER 7, 1994



# KEELE VALLEY LANDFILL CH4 STUDY

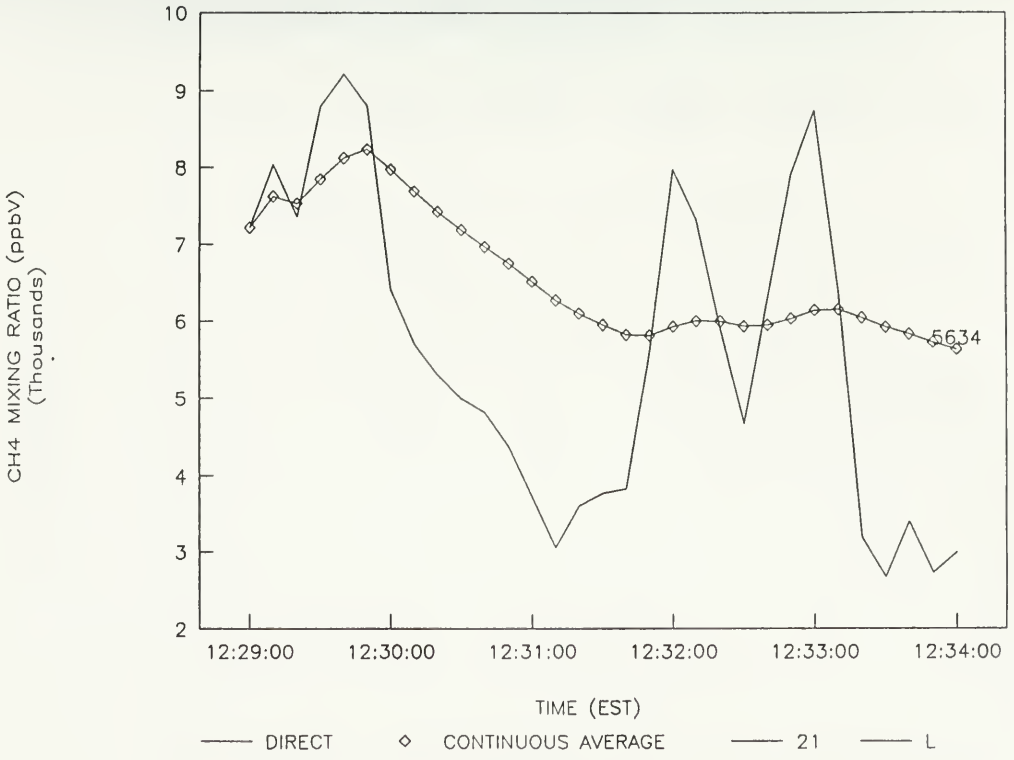
DATE : OCTOBER 23, 1994




KEELE VALLEY LANDFILL CH4 STUDY
DATE : OCTOBER 23, 1994
CH4 MIXING RATIO (ppbV)
(Thousands)
31
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
23754
14:40:00
14:41:00
14:42:00
14:43:00
14:44:00
14:45:00
TIME (EST)
DIRECT
CONTINUOUS AVERAGE
20
H

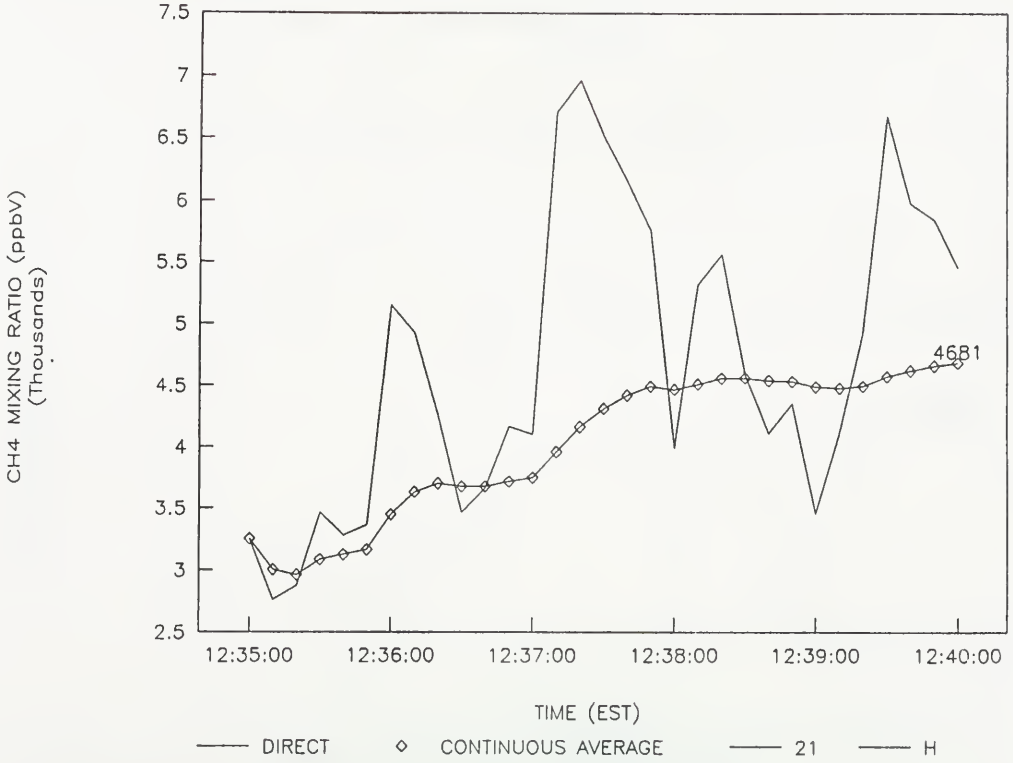
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 7, 1994



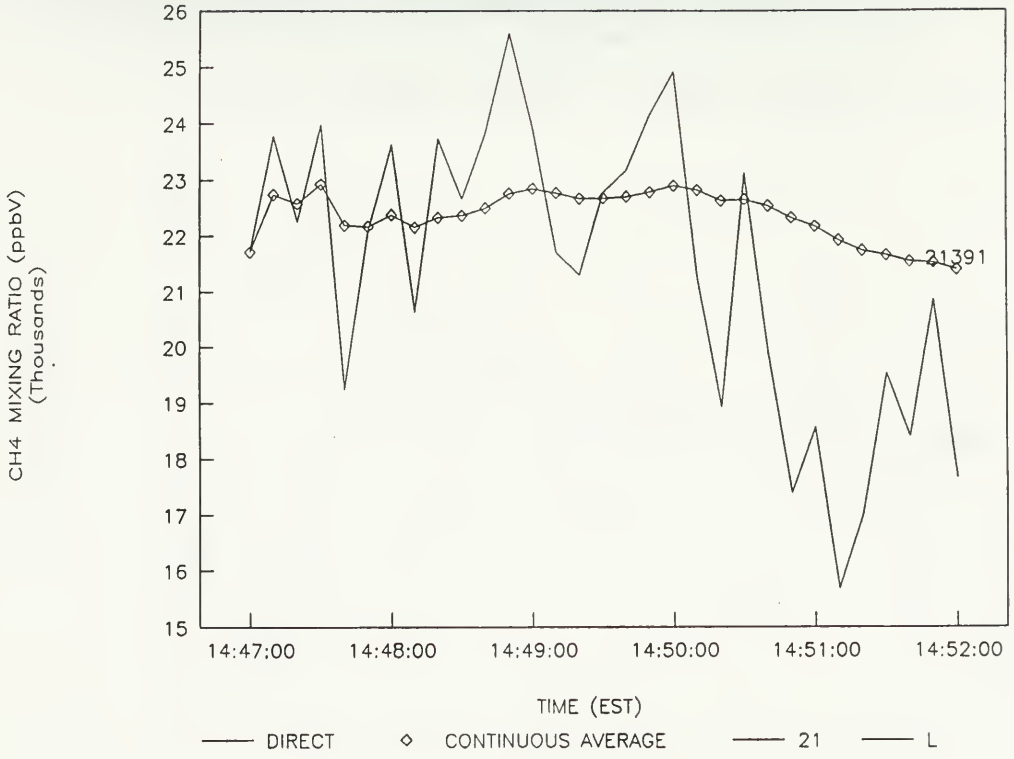
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 7, 1994



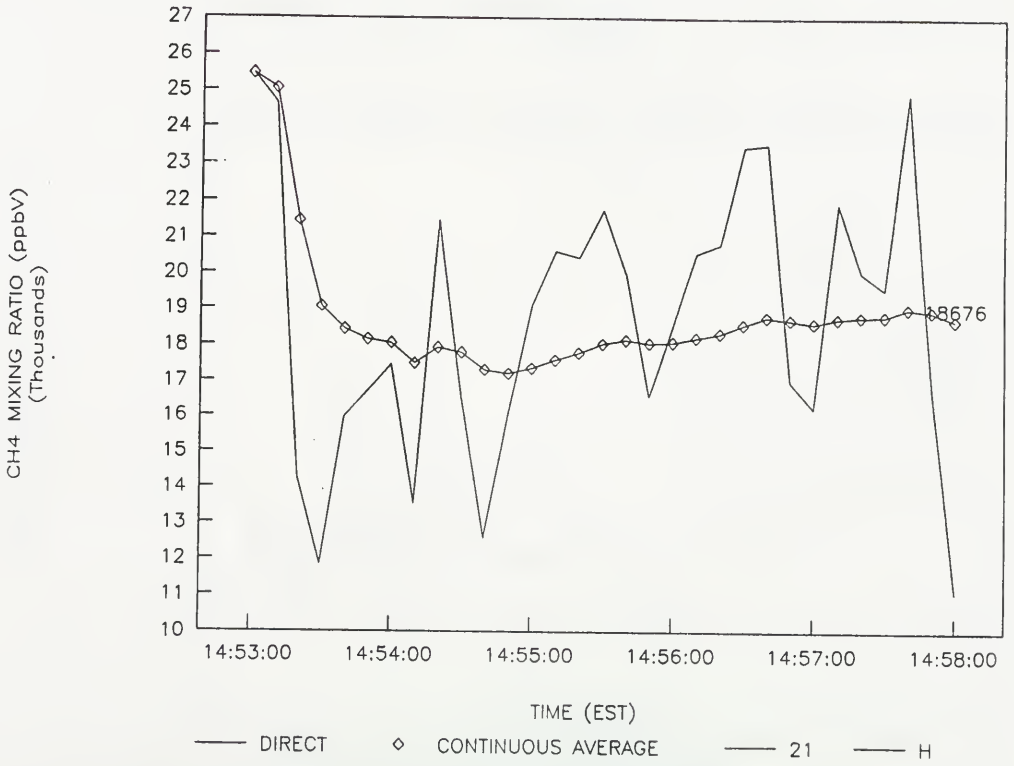
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 23, 1994



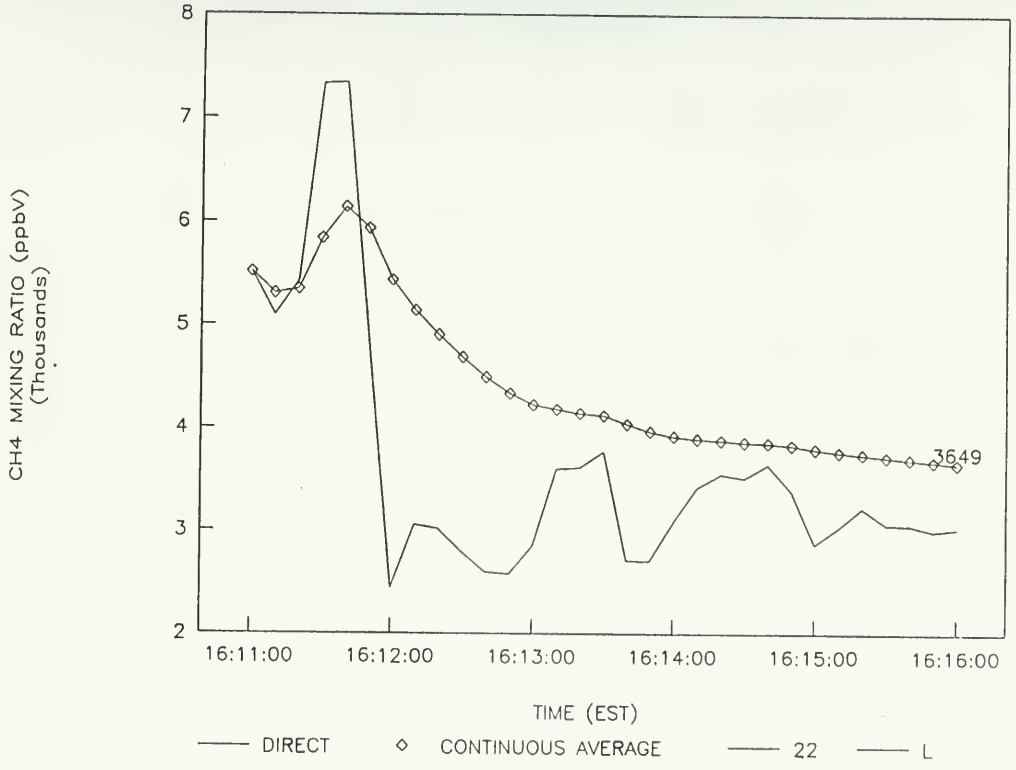
# KEELE VALLEY LANDFILL CH4 STUDY

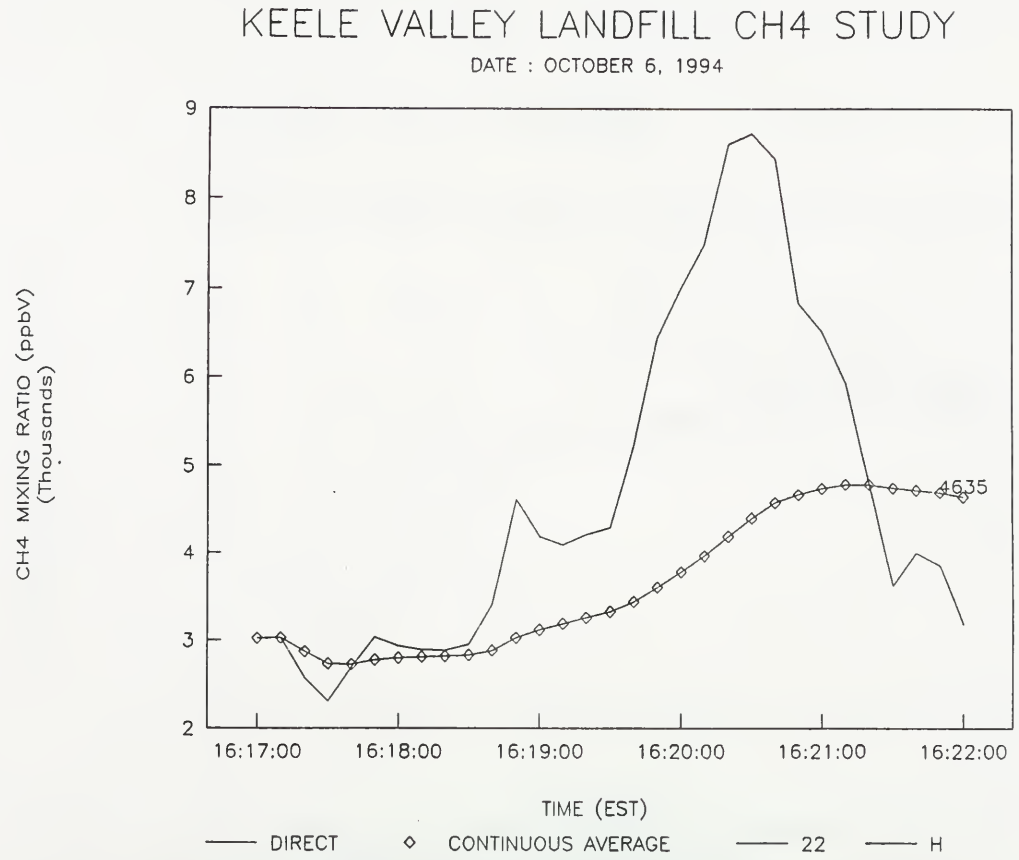
DATE : OCTOBER 23, 1994



# KEELE VALLEY LANDFILL CH4 STUDY

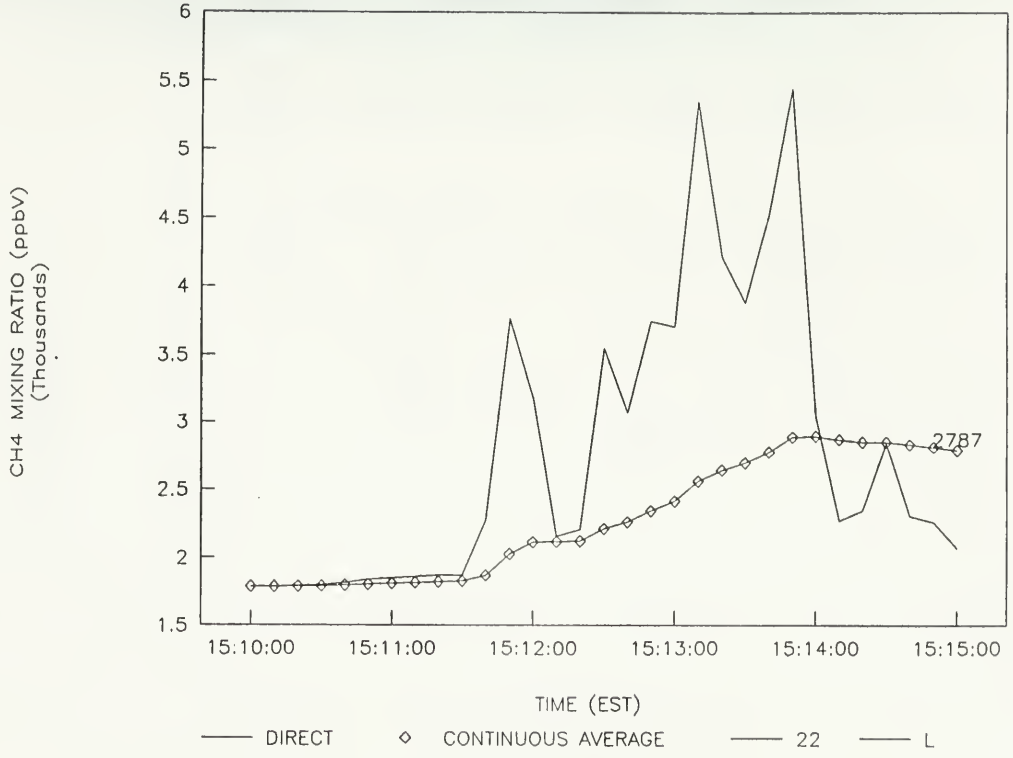
DATE : OCTOBER 6, 1994




KEELE VALLEY LANDFILL CH4 STUDY
DATE : OCTOBER 6, 1994
CH4 MIXING RATIO (ppbV)
(Thousands)
9
8
7
6
5
4
3
2
4635
16:17:00
16:18:00
16:19:00
16:20:00
16:21:00
16:22:00
TIME (EST)
DIRECT
CONTINUOUS AVERAGE
22
H

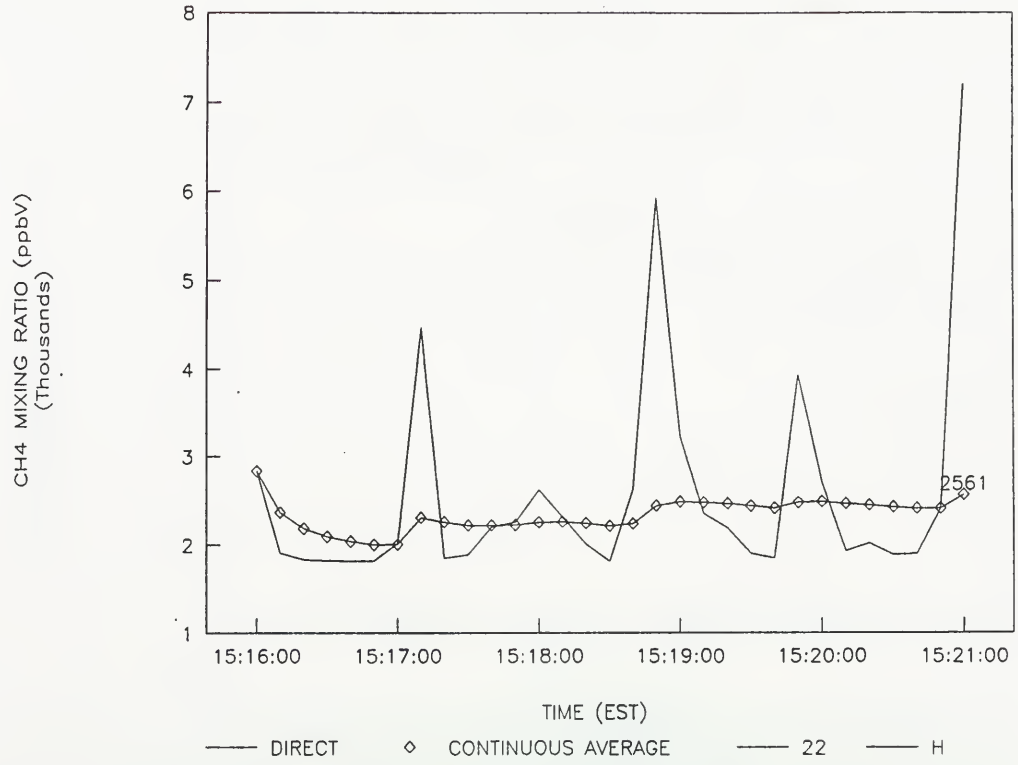
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



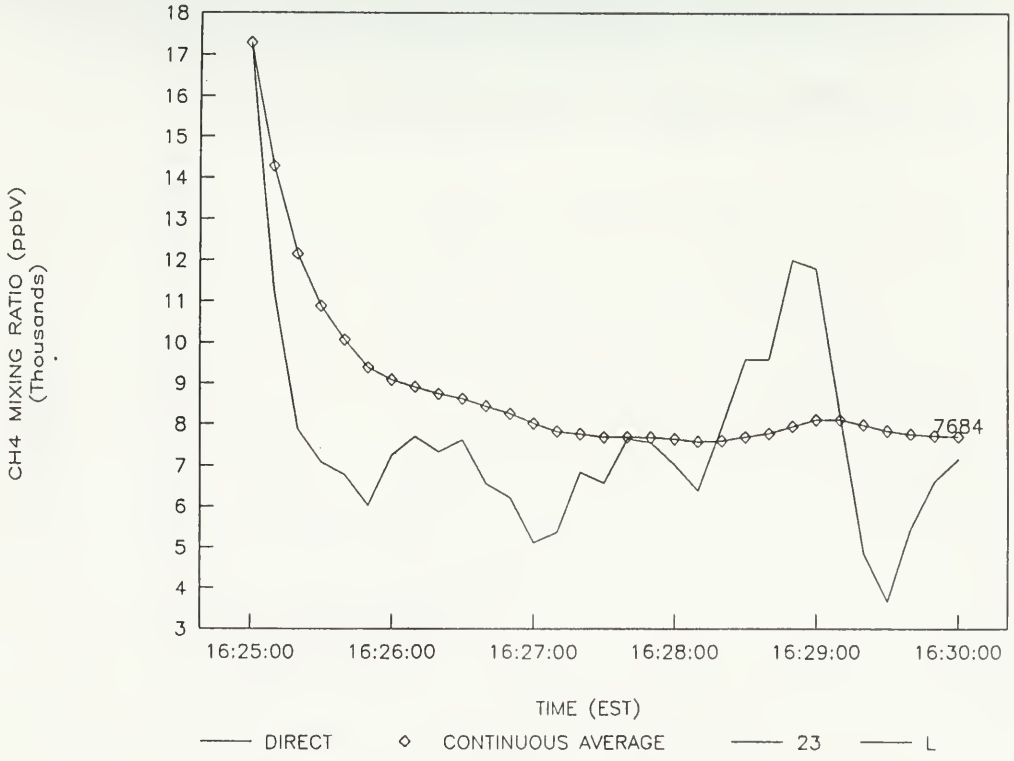
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



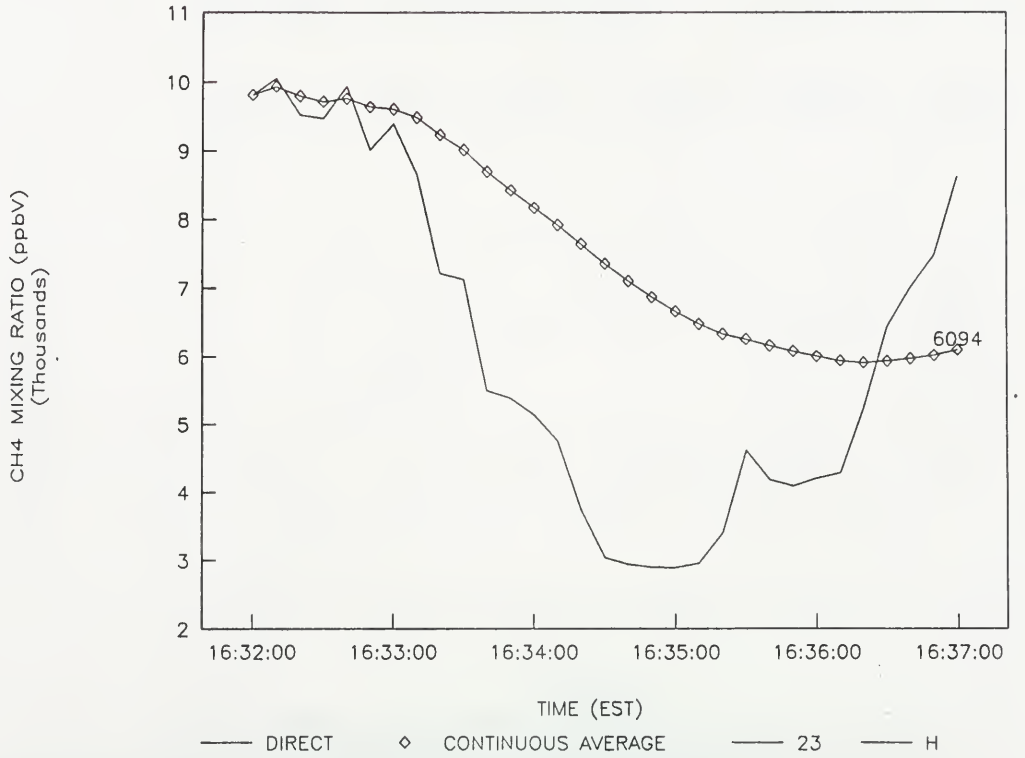
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



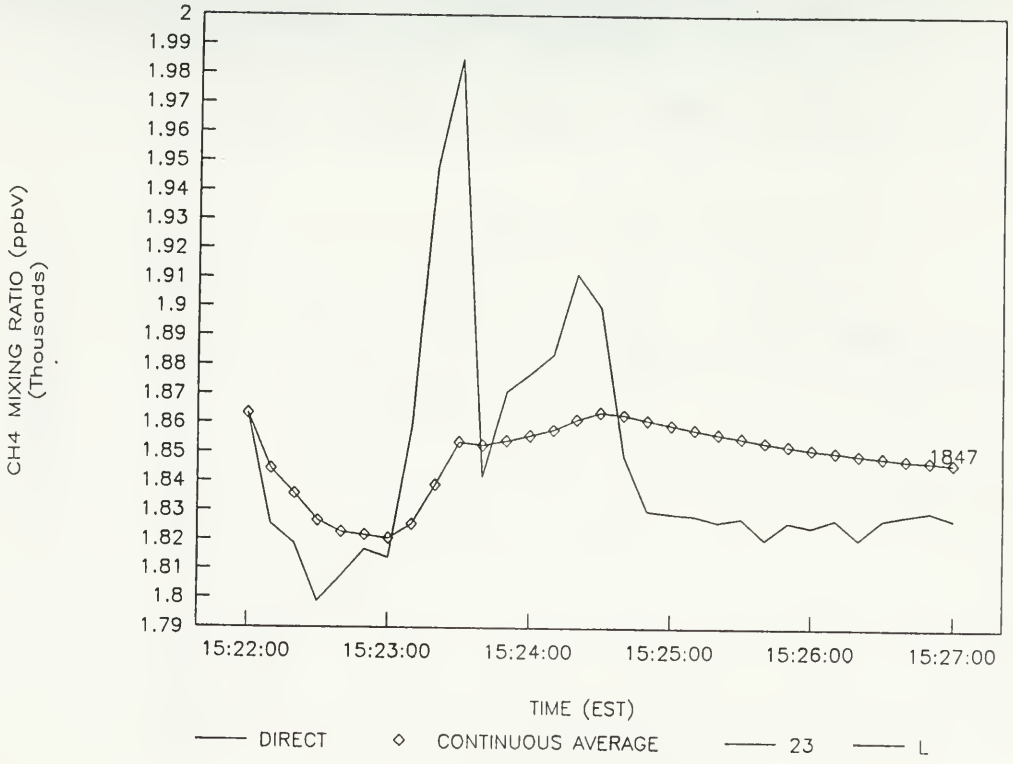
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



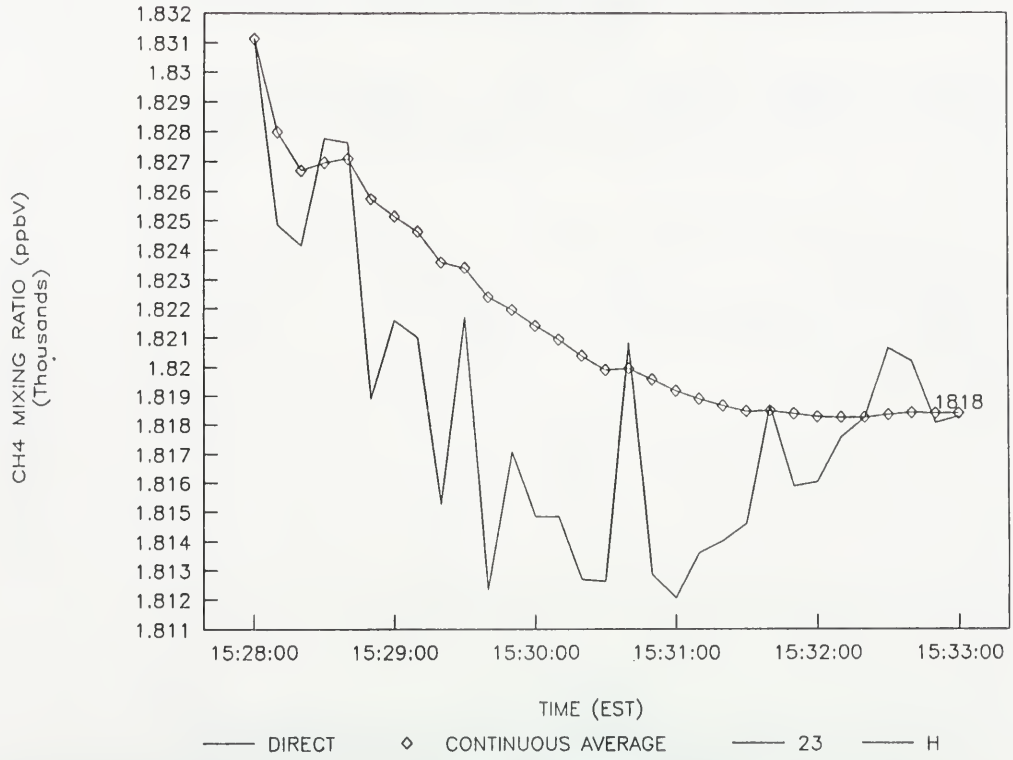
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



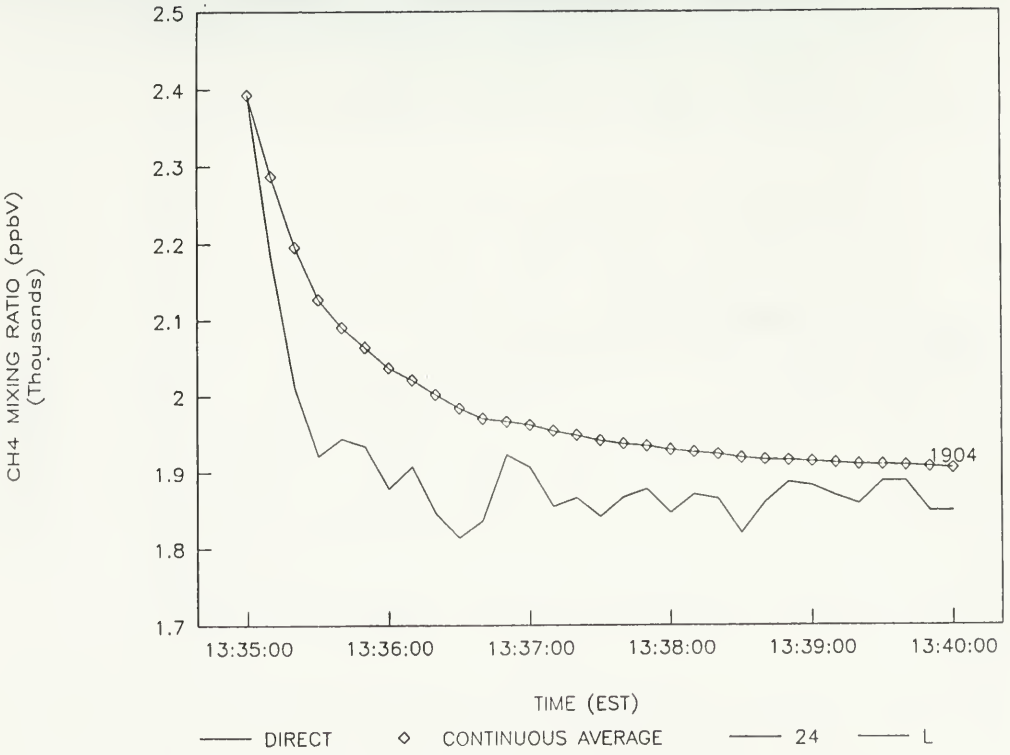
# KEELE VALLEY LANDFILL CH4 STUDY

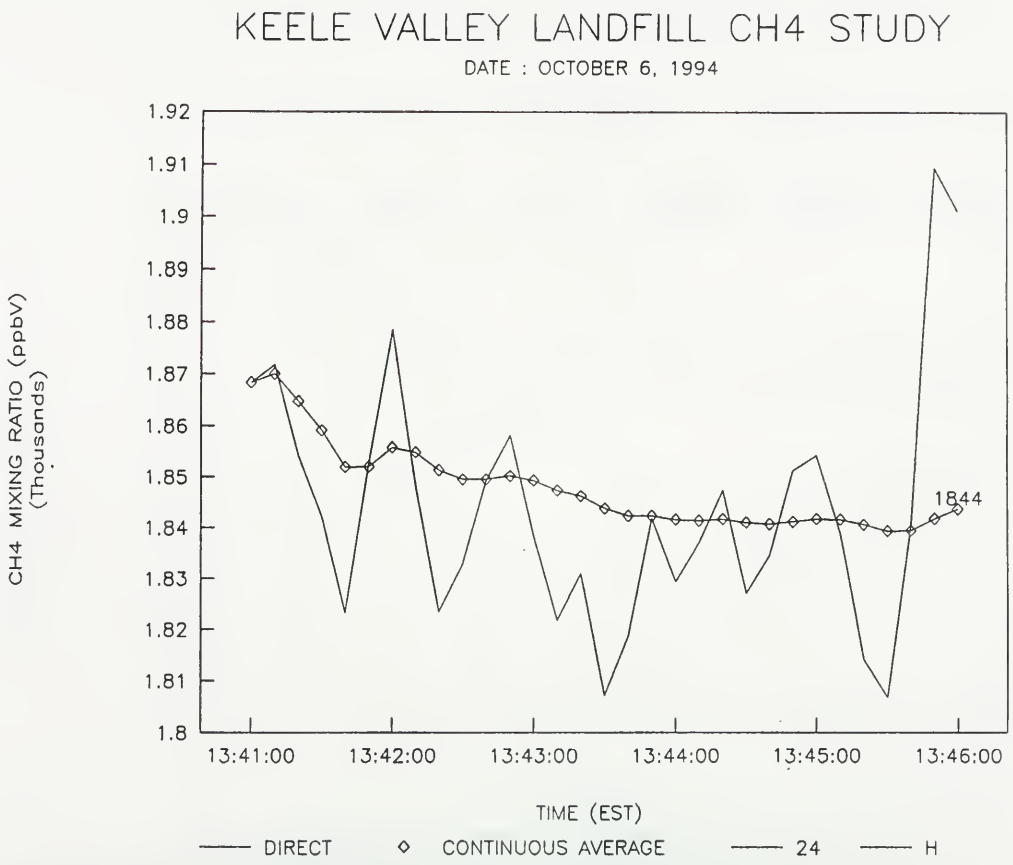
DATE : OCTOBER 12, 1994



# KEELE VALLEY LANDFILL CH4 STUDY

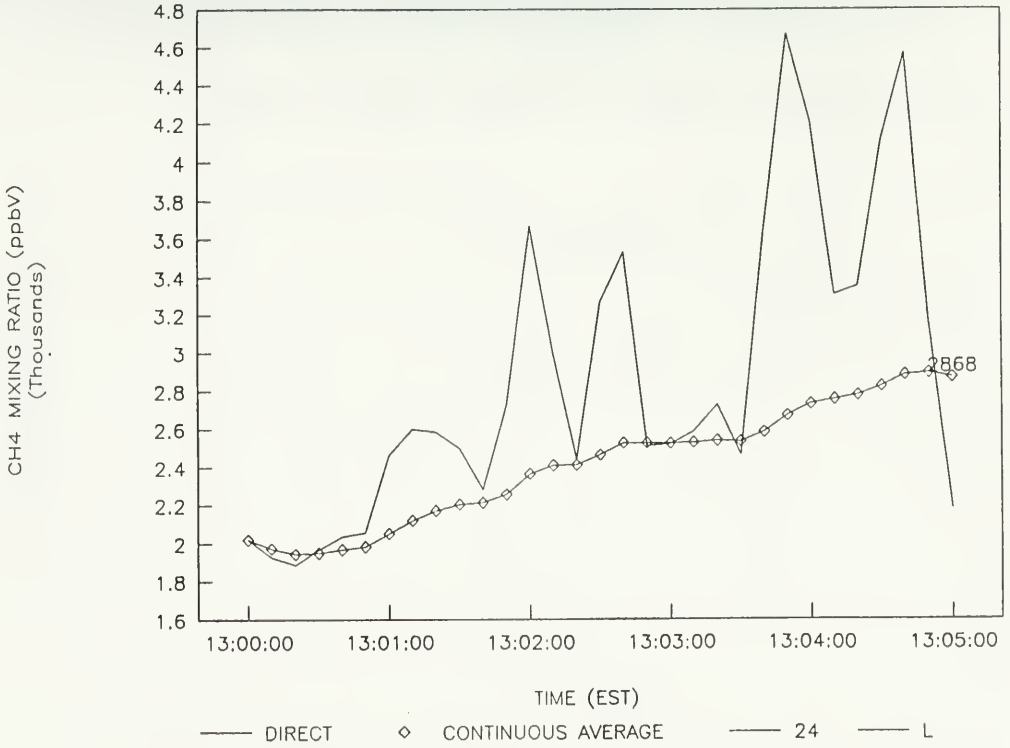
DATE : OCTOBER 6, 1994

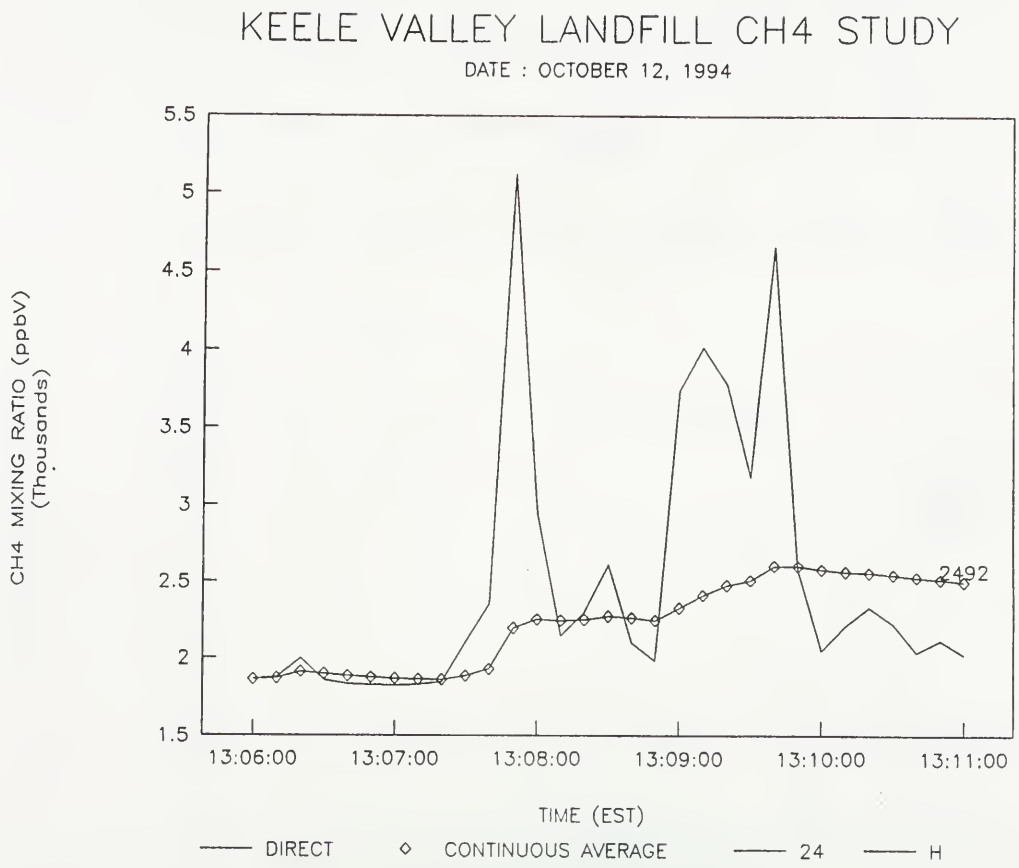



KEELE VALLEY LANDFILL CH4 STUDY
DATE : OCTOBER 6, 1994
CH4 MIXING RATIO (ppbV)
(Thousands)
1.92
1.91
1.9
1.89
1.88
1.87
1.86
1.85
1.84
1.83
1.82
1.81
1.8
1844
13:41:00
13:42:00
13:43:00
13:44:00
13:45:00
13:46:00
TIME (EST)
DIRECT
CONTINUOUS AVERAGE
24
H

# KEELE VALLEY LANDFILL CH4 STUDY

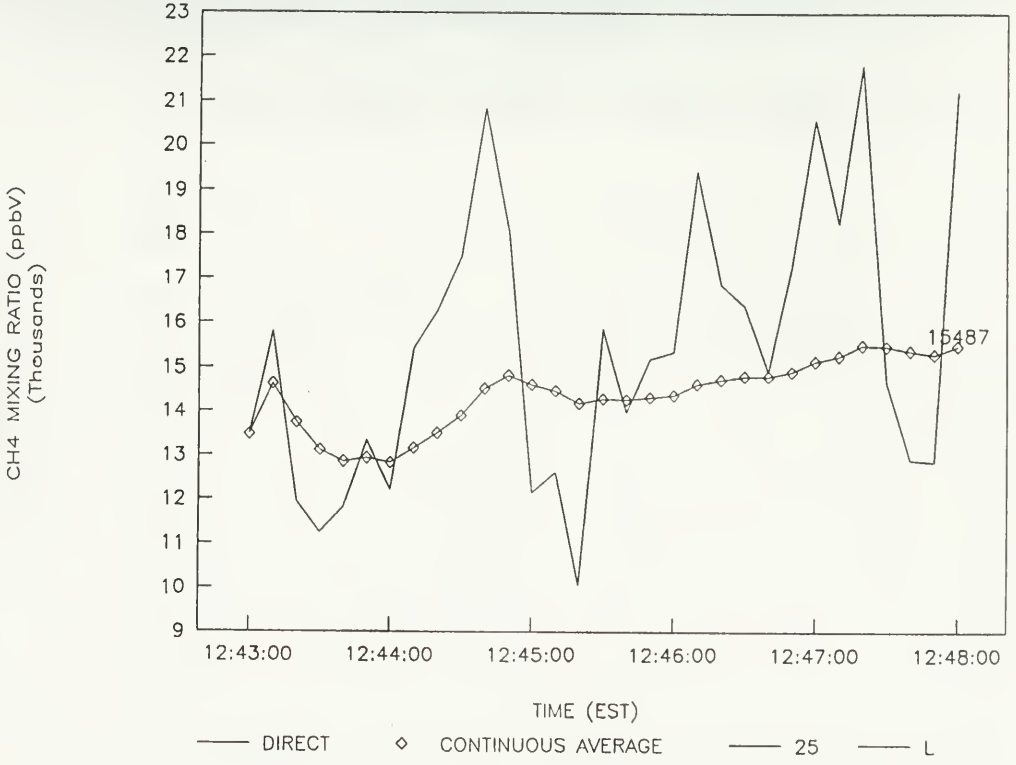
DATE : OCTOBER 12, 1994

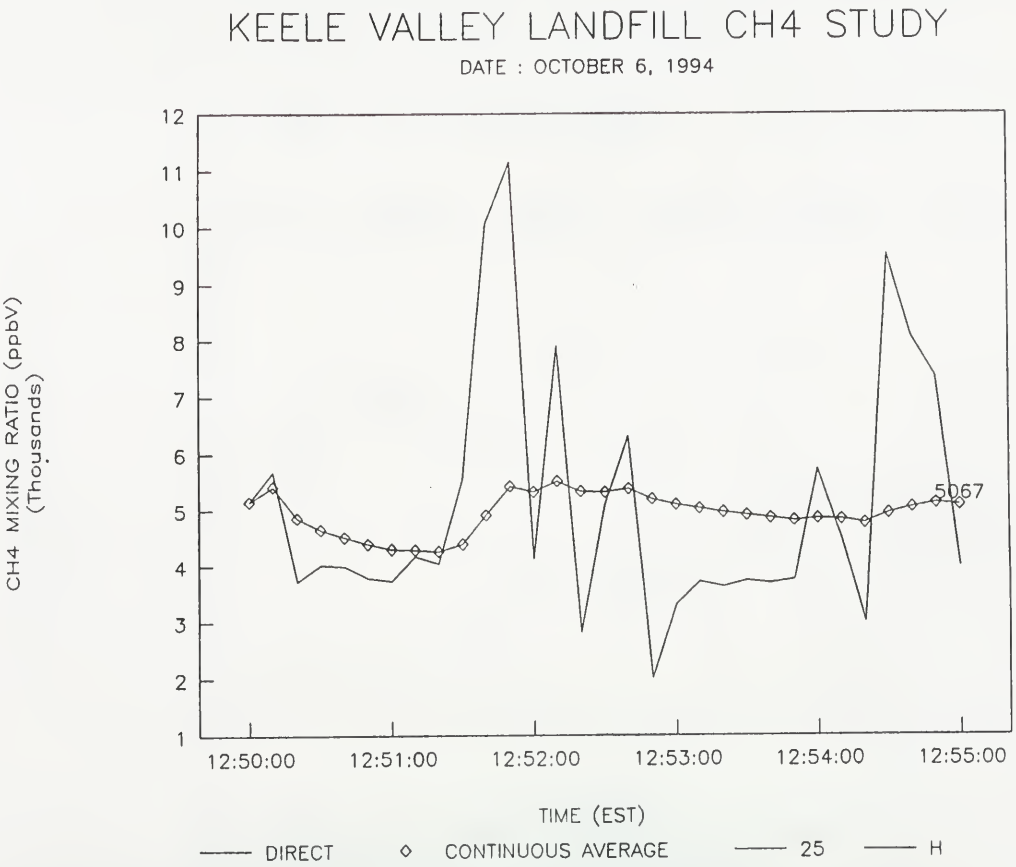



KEELE VALLEY LANDFILL CH4 STUDY
DATE : OCTOBER 12, 1994
CH4 MIXING RATIO (ppbV)
(Thousands)
5.5
5
4.5
4
3.5
3
2.5
2
1.5
13:06:00
13:07:00
13:08:00
13:09:00
13:10:00
13:11:00
2492
TIME (EST)
DIRECT
CONTINUOUS AVERAGE
24
H

# KEELE VALLEY LANDFILL CH4 STUDY

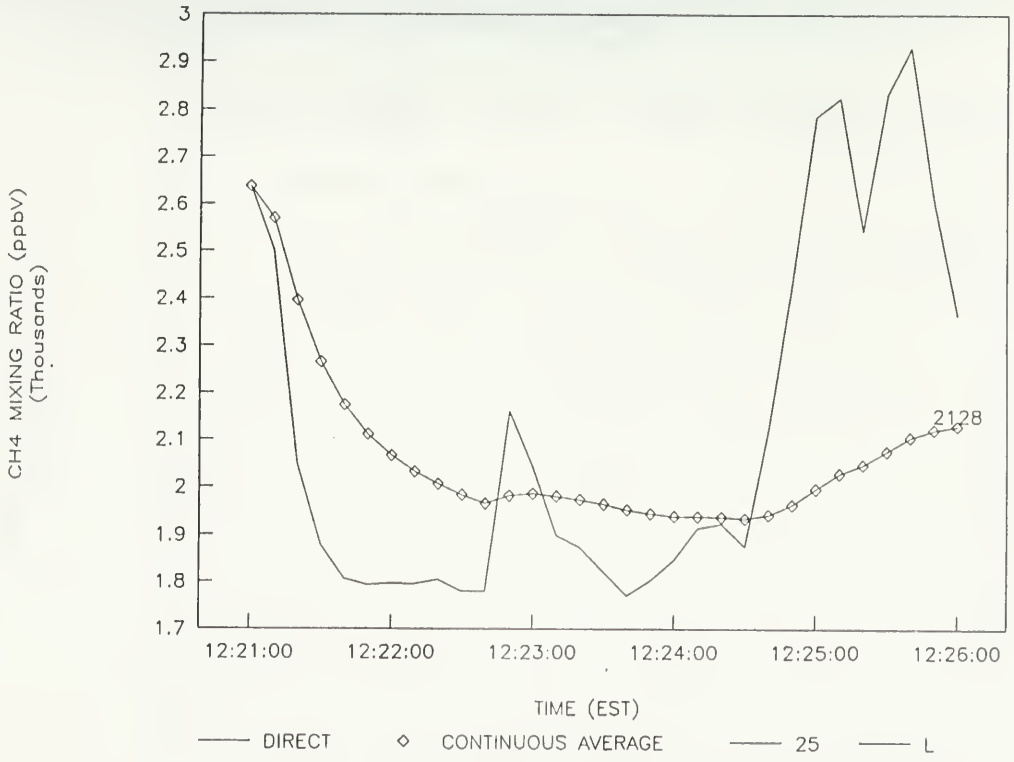
DATE : OCTOBER 6, 1994




KEELE VALLEY LANDFILL CH4 STUDY
DATE : OCTOBER 6, 1994
CH4 MIXING RATIO (ppbV)
(Thousands)
12
11
10
9
8
7
6
5
4
3
2
1
5067
12:50:00
12:51:00
12:52:00
12:53:00
12:54:00
12:55:00
TIME (EST)
DIRECT
CONTINUOUS AVERAGE
25
H

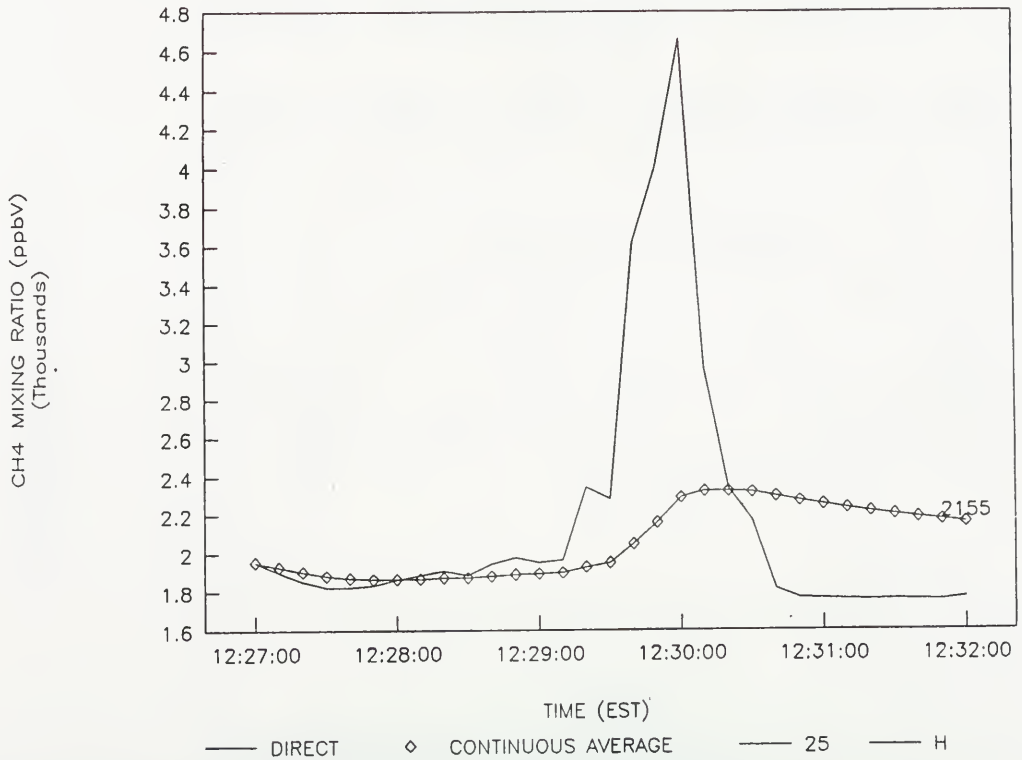
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



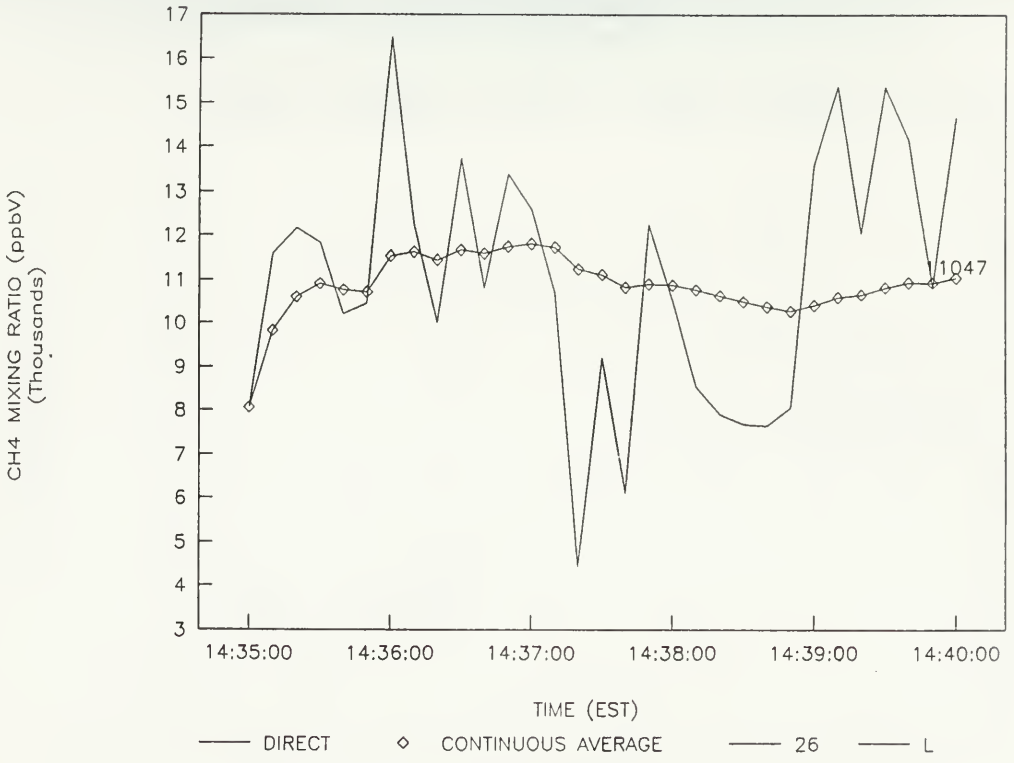
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



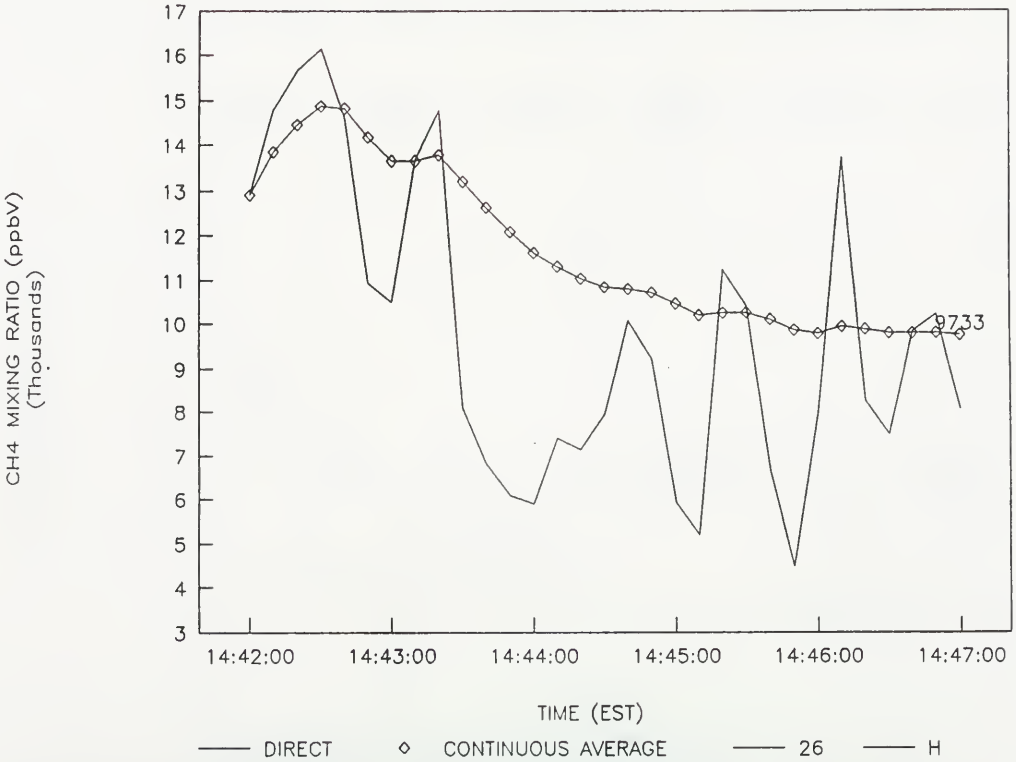
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 7, 1994



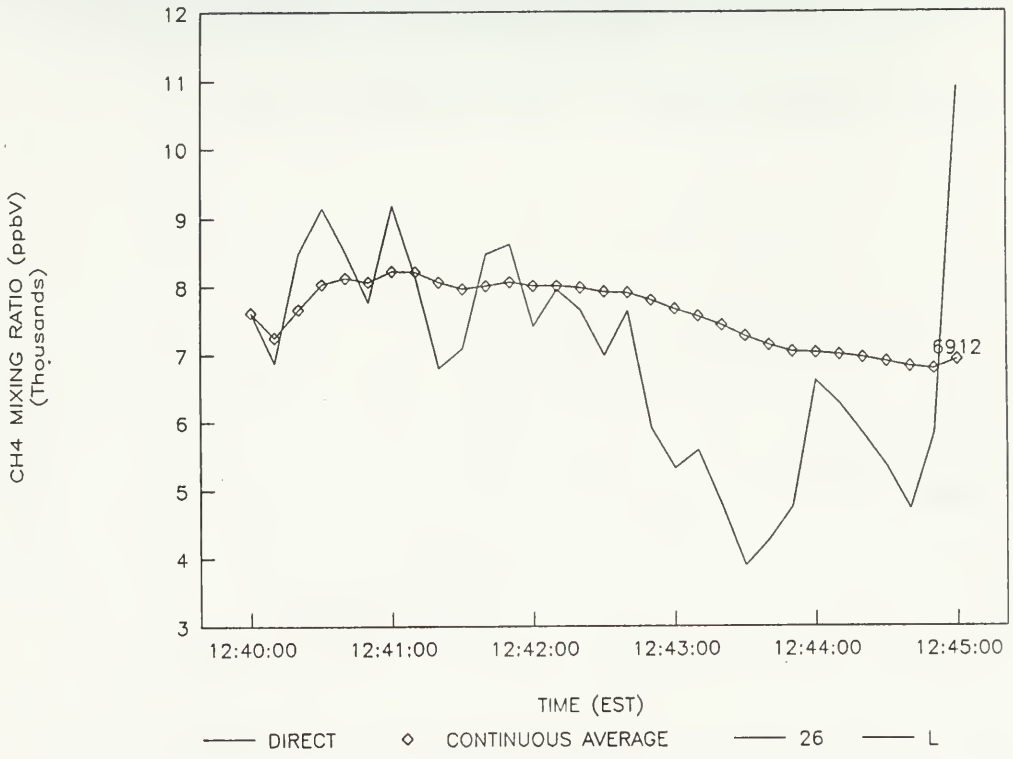
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 7, 1994



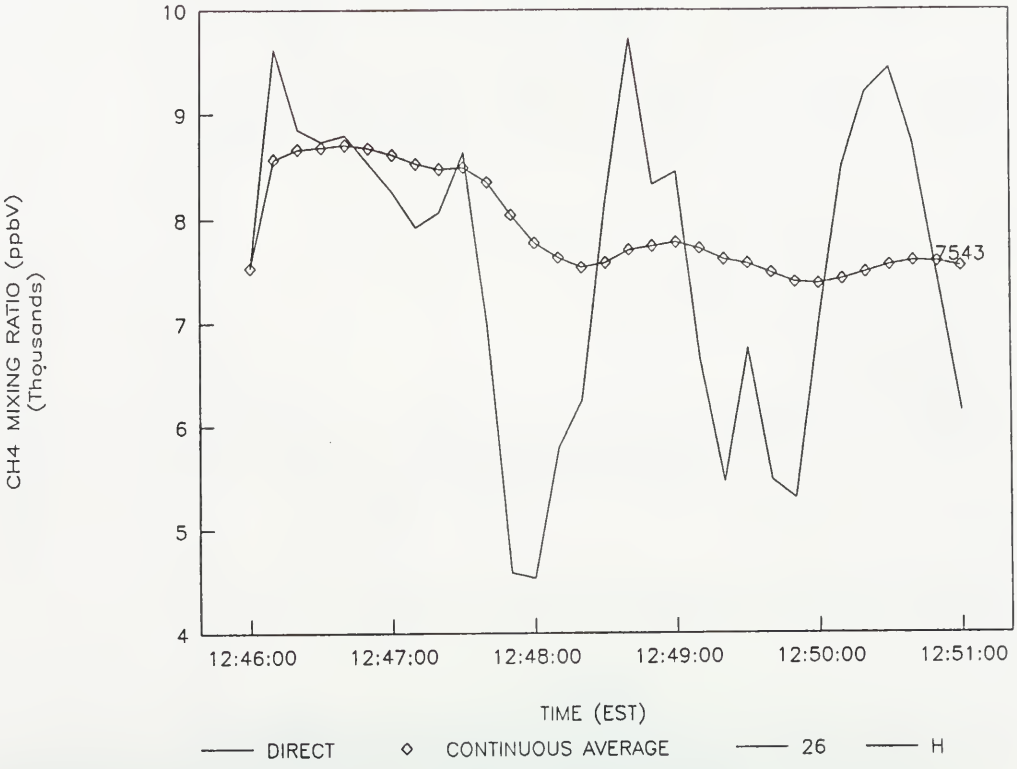
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 23, 1994



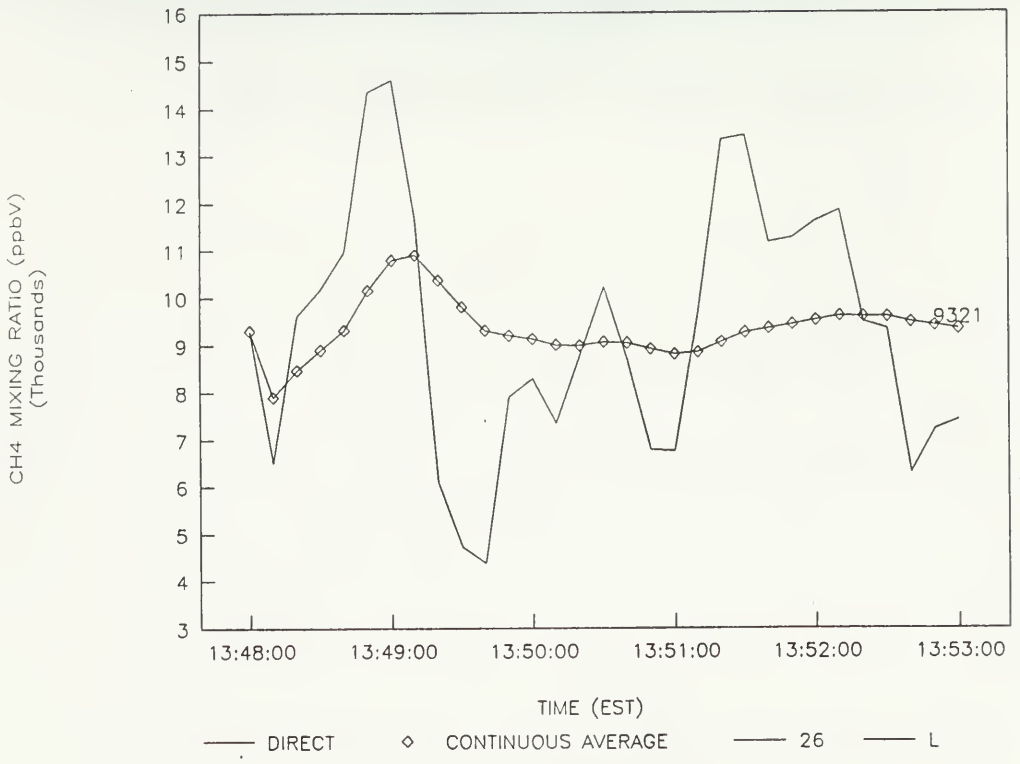
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 23, 1994



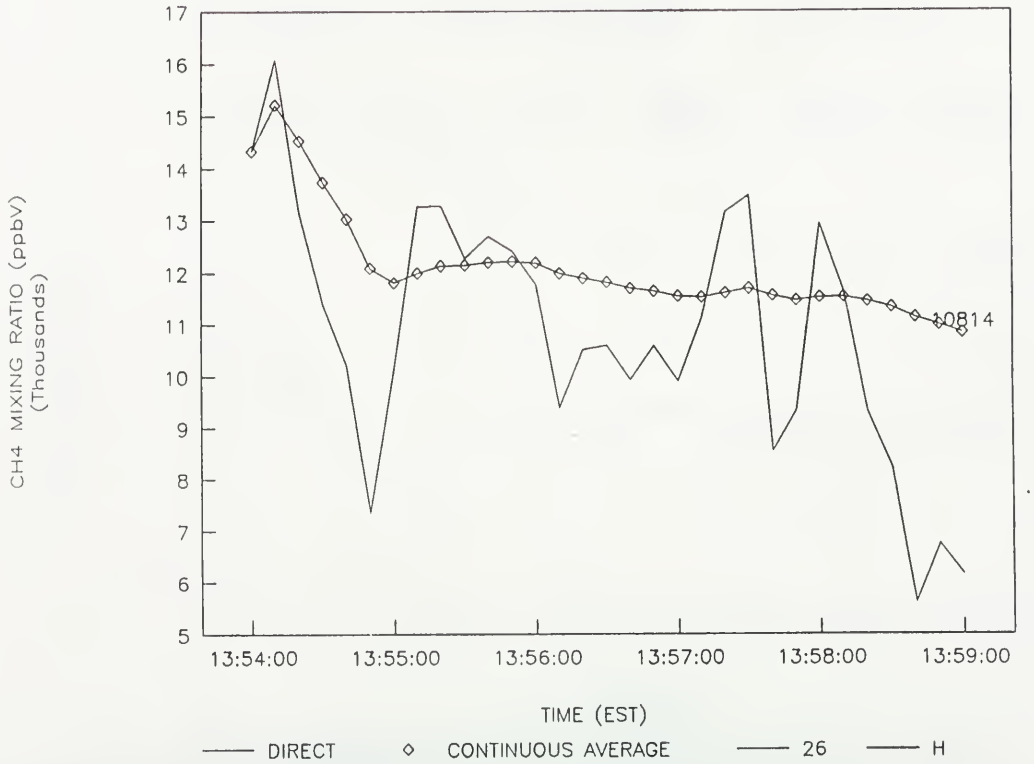
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 23, 1994



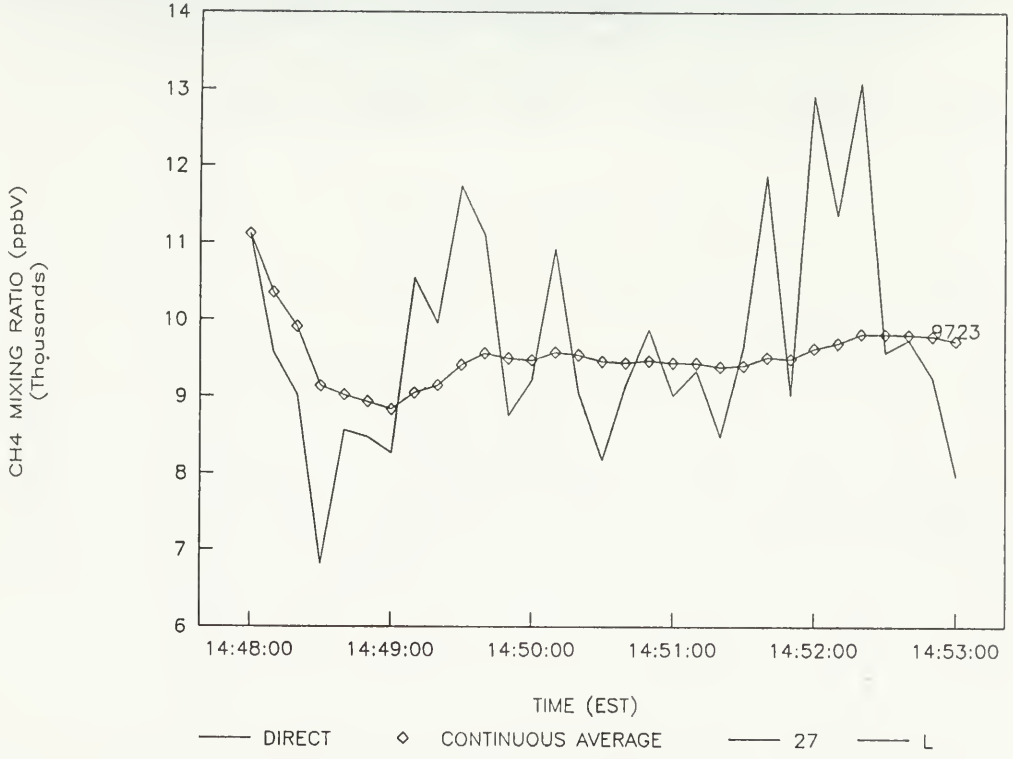
# KEELE VALLEY LANDFILL CH4 STUDY

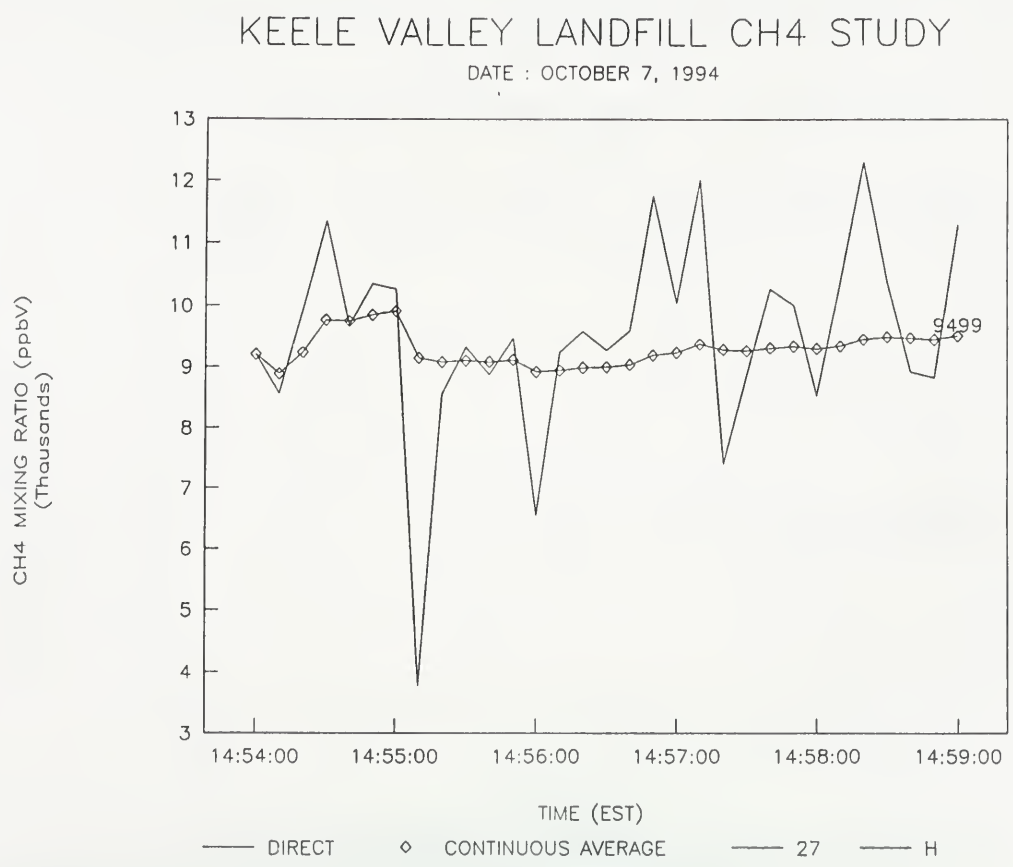
DATE : OCTOBER 23, 1994



# KEELE VALLEY LANDFILL CH4 STUDY

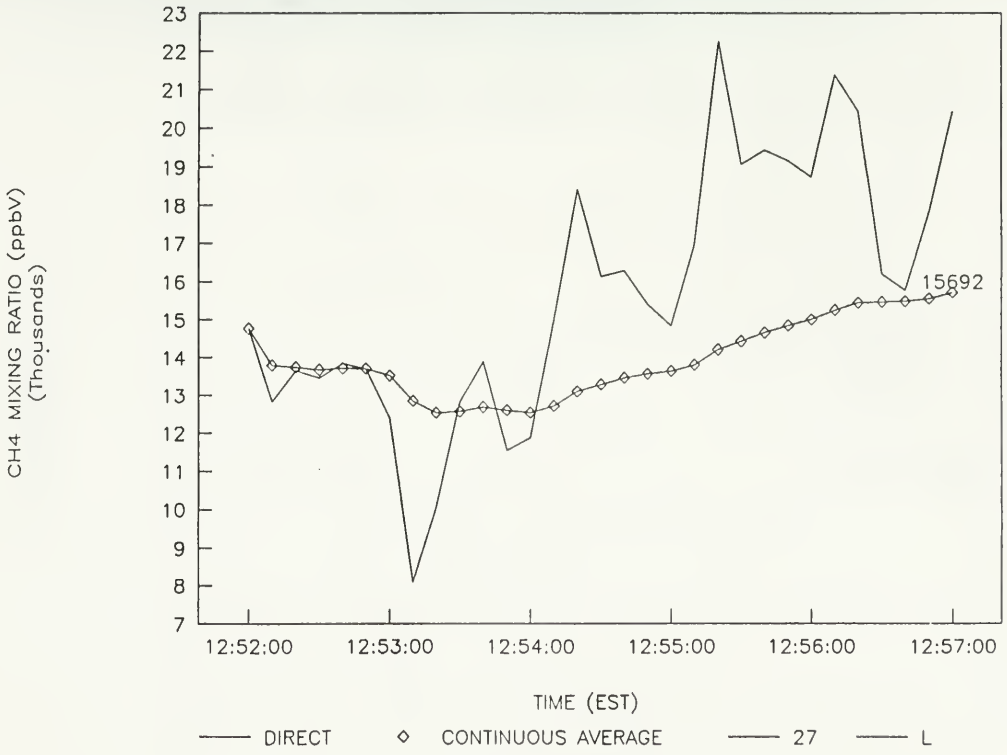
DATE : OCTOBER 7, 1994




KEELE VALLEY LANDFILL CH4 STUDY
DATE : OCTOBER 7, 1994
CH4 MIXING RATIO (ppbV)
(Thousands)
13
12
11
10
9
8
7
6
5
4
3
9499
14:54:00
14:55:00
14:56:00
14:57:00
14:58:00
14:59:00
TIME (EST)
DIRECT
CONTINUOUS AVERAGE
27
H

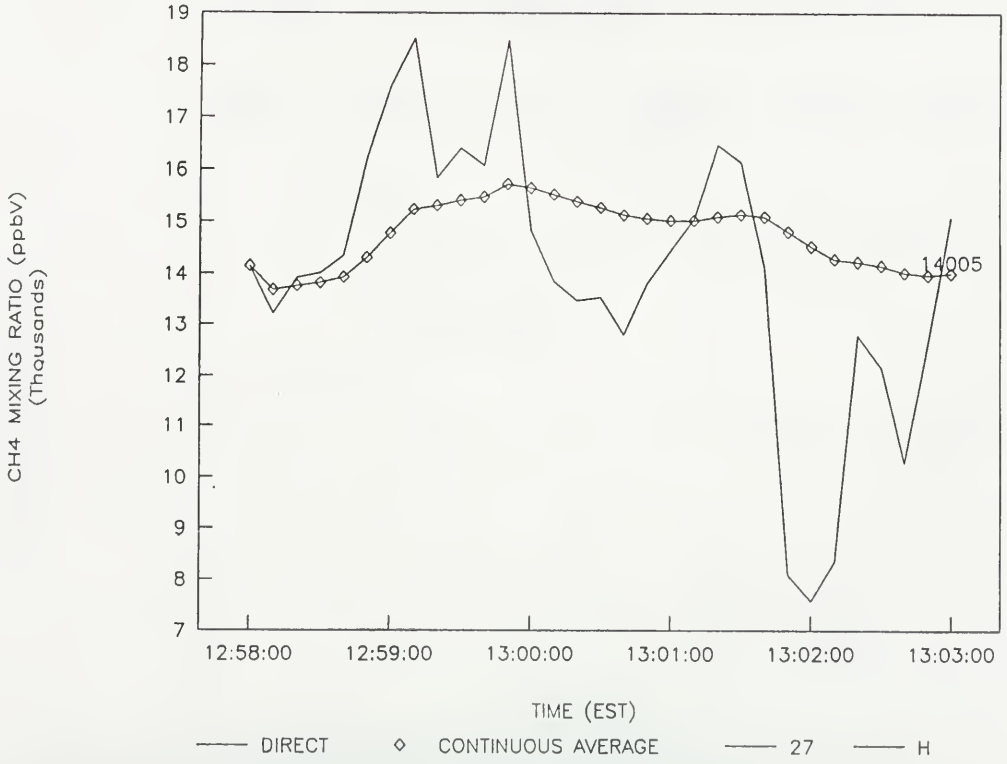
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 23, 1994



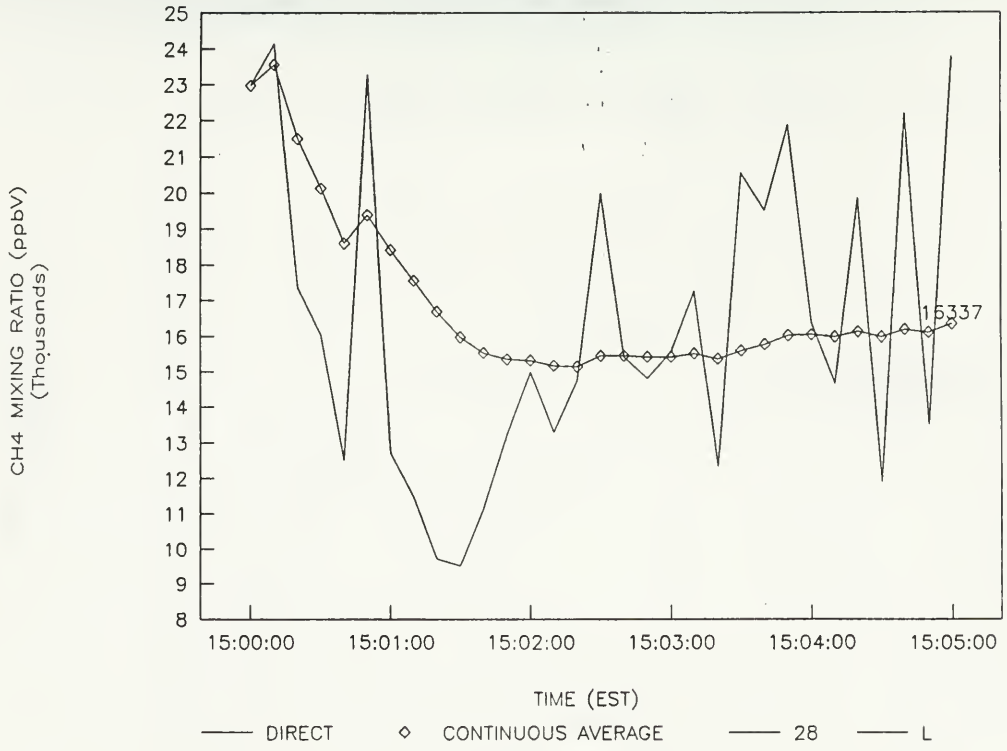
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 23, 1994



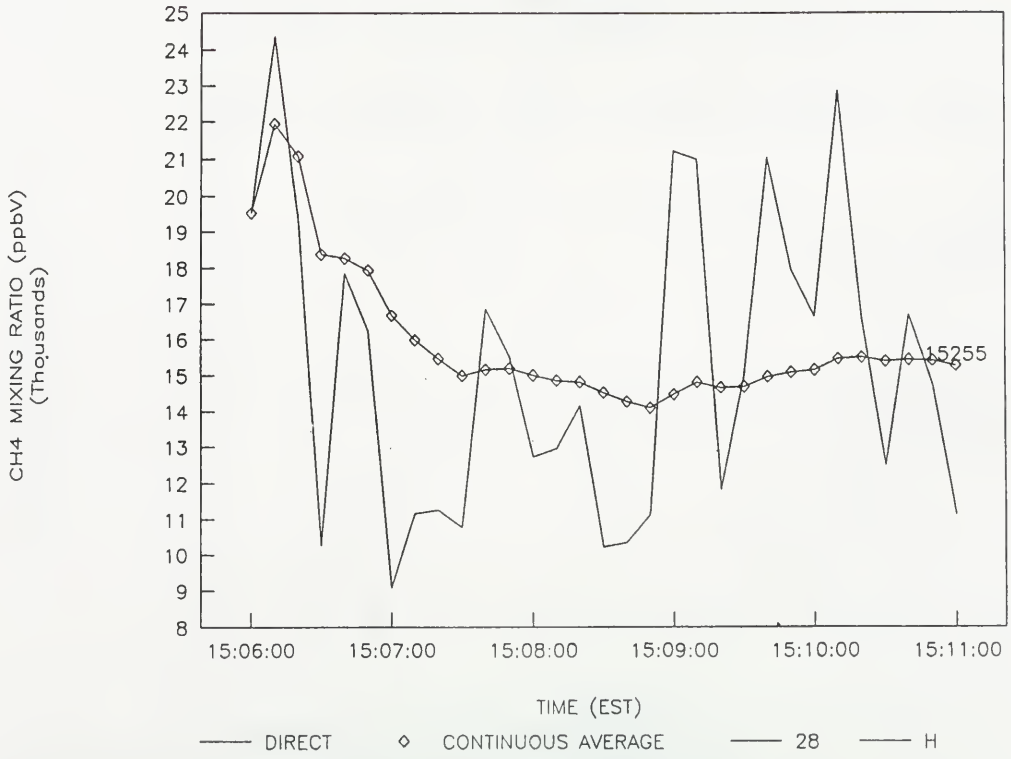
# KEELE VALLEY LANDFILL CH4 STUDY

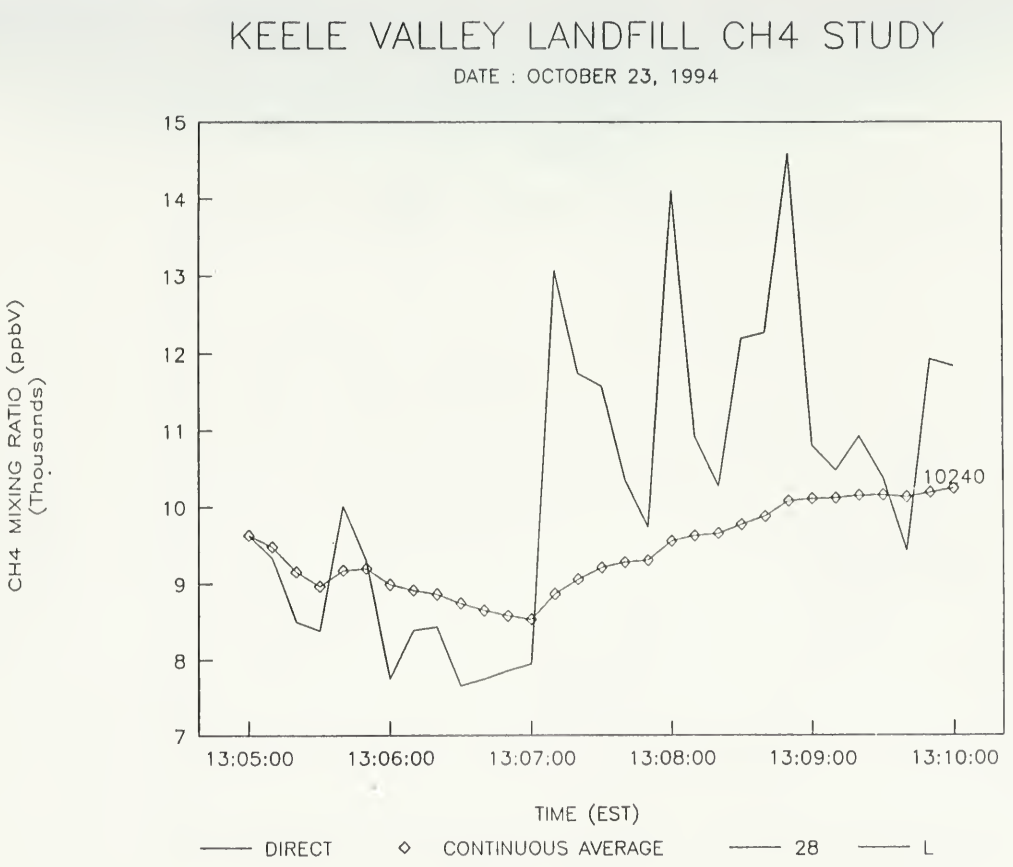
DATE : OCTOBER 7, 1994



# KEELE VALLEY LANDFILL CH4 STUDY

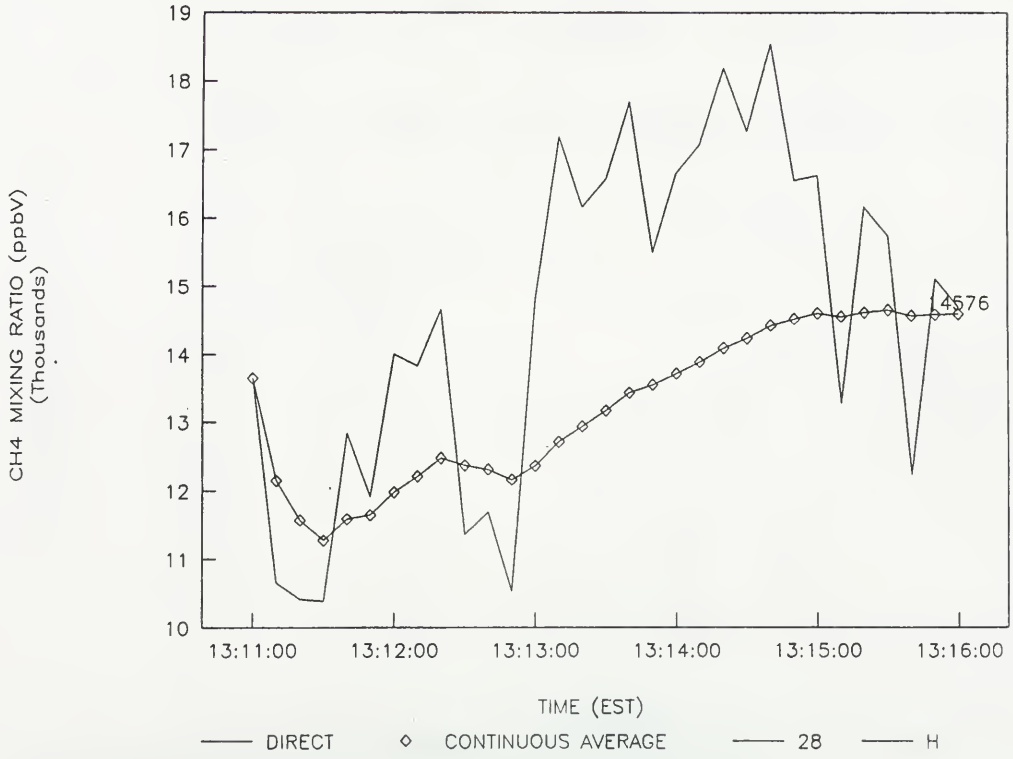
DATE : OCTOBER 7, 1994

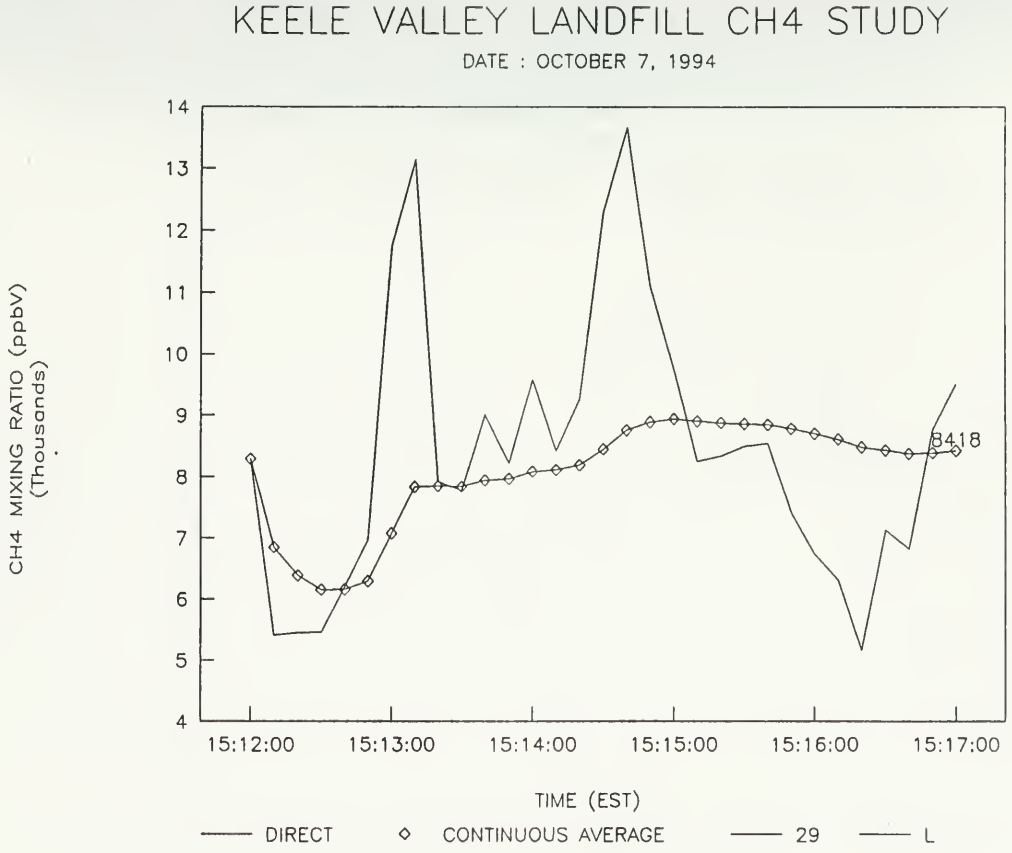



KEELE VALLEY LANDFILL CH4 STUDY
DATE : OCTOBER 23, 1994
CH4 MIXING RATIO (ppbV)
(Thousands)
15
14
13
12
11
10
9
8
7
13:05:00
13:06:00
13:07:00
13:08:00
13:09:00
13:10:00
10240
TIME (EST)
DIRECT
CONTINUOUS AVERAGE
28
L

# KEELE VALLEY LANDFILL CH4 STUDY

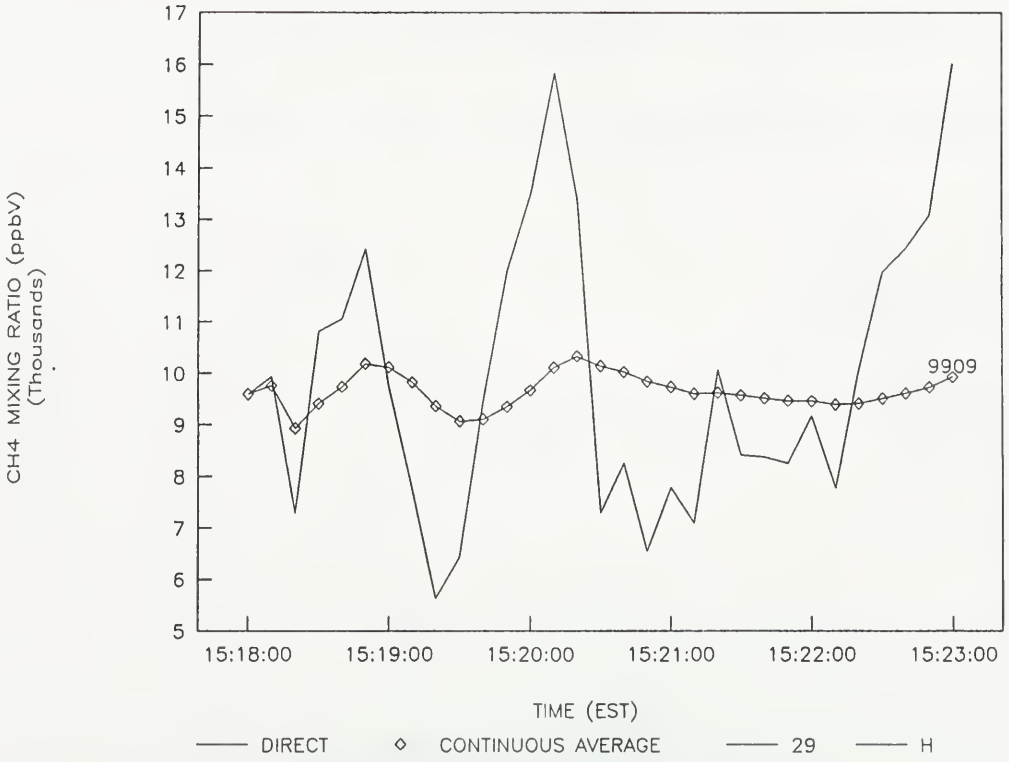
DATE : OCTOBER 23, 1994




KEELE VALLEY LANDFILL CH4 STUDY
DATE : OCTOBER 7, 1994
CH4 MIXING RATIO (ppbV)
(Thousands)
14
13
12
11
10
9
8
7
6
5
4
8418
15:12:00
15:13:00
15:14:00
15:15:00
15:16:00
15:17:00
TIME (EST)
DIRECT
CONTINUOUS AVERAGE
29
L

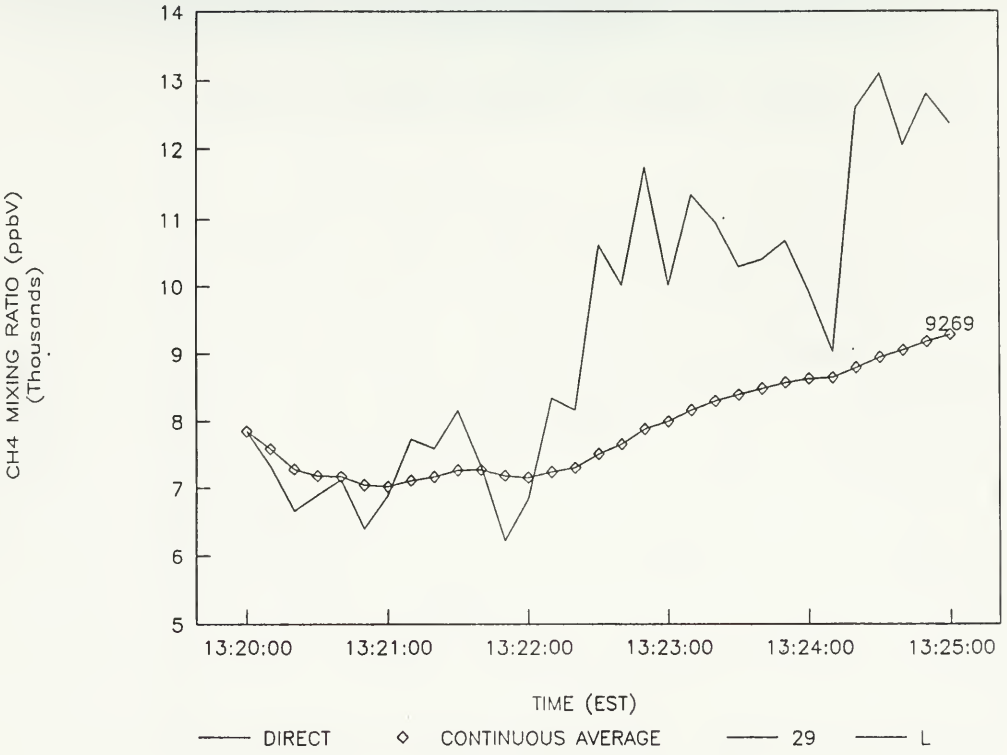
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 7, 1994



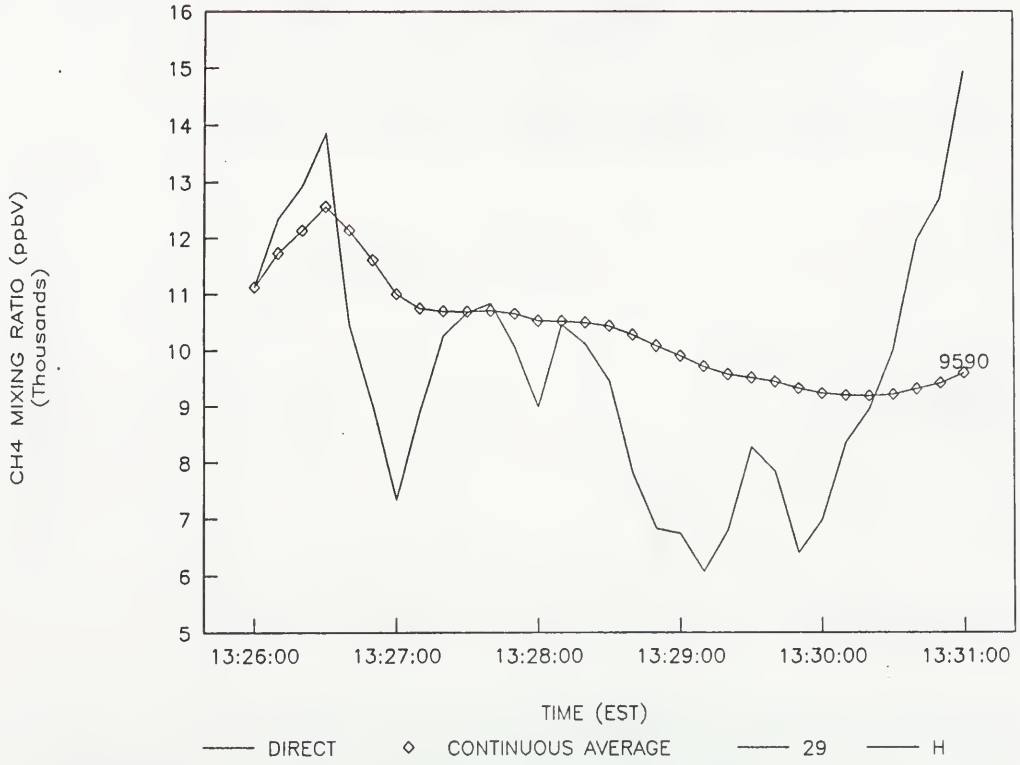
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 23, 1994



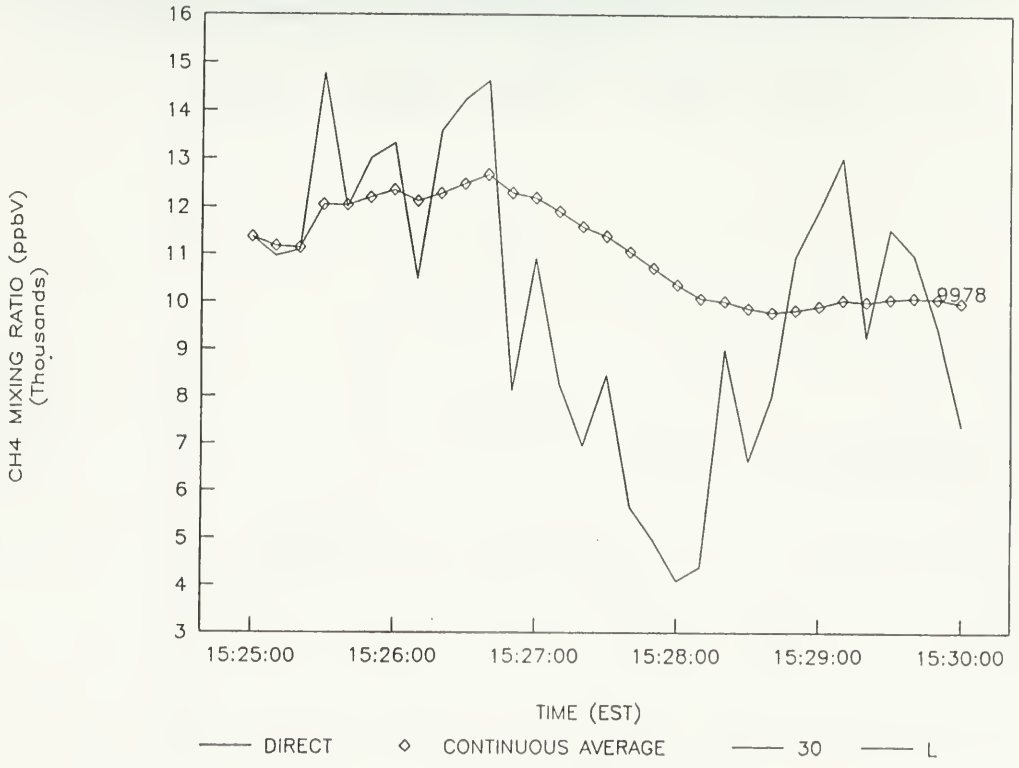
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 23, 1994



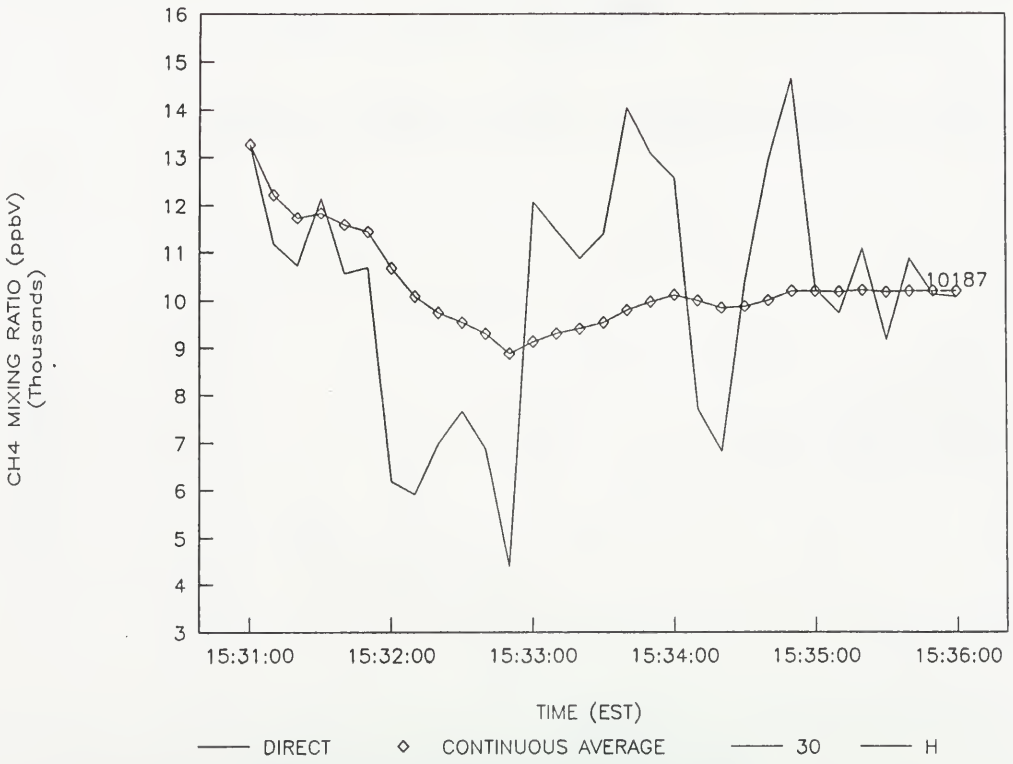
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 7, 1994



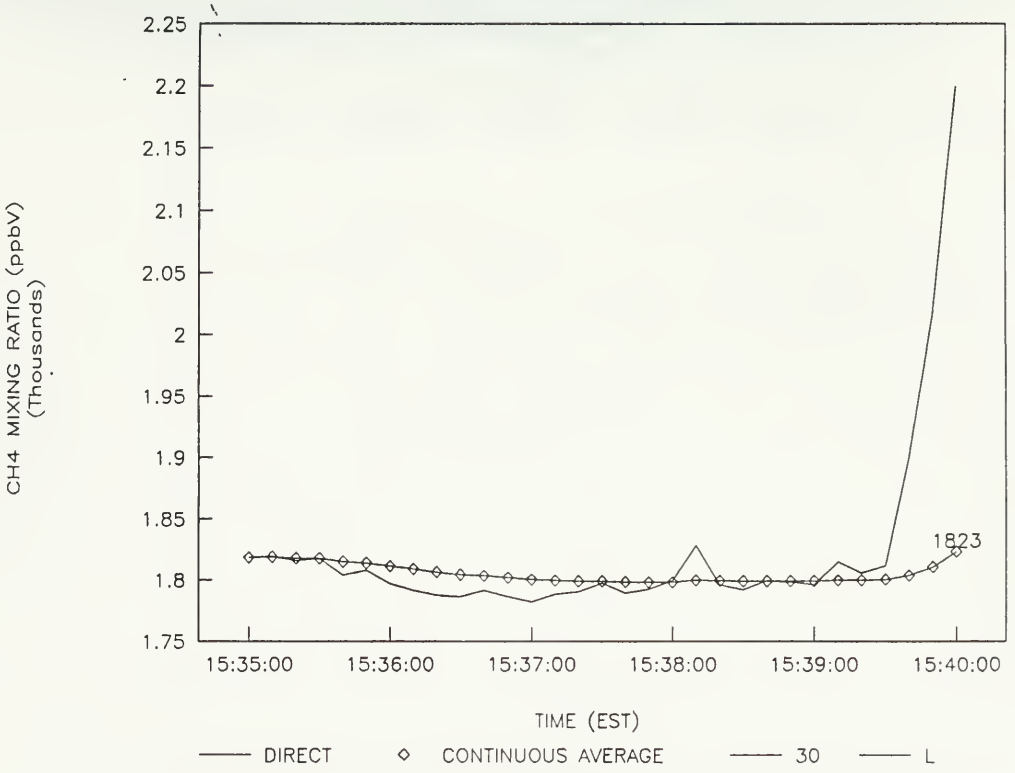
# KEELE VALLEY LANDFILL CH4 STUDY

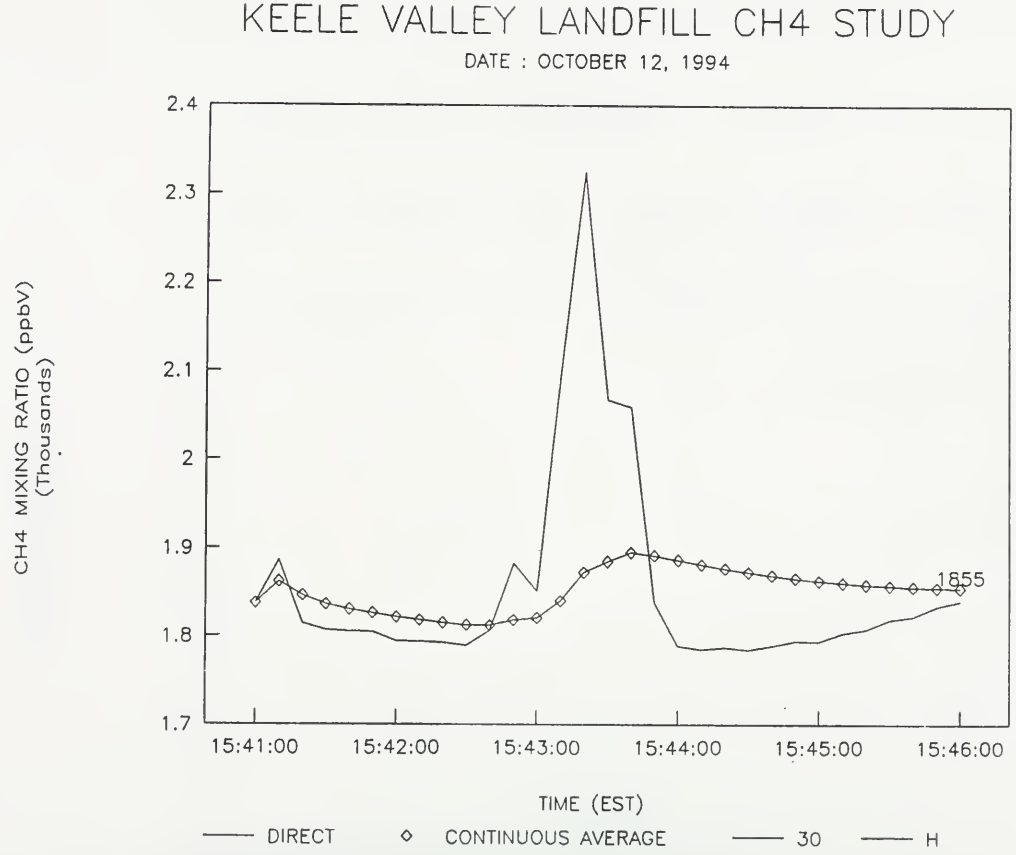
DATE : OCTOBER 7, 1994



# KEELE VALLEY LANDFILL CH4 STUDY

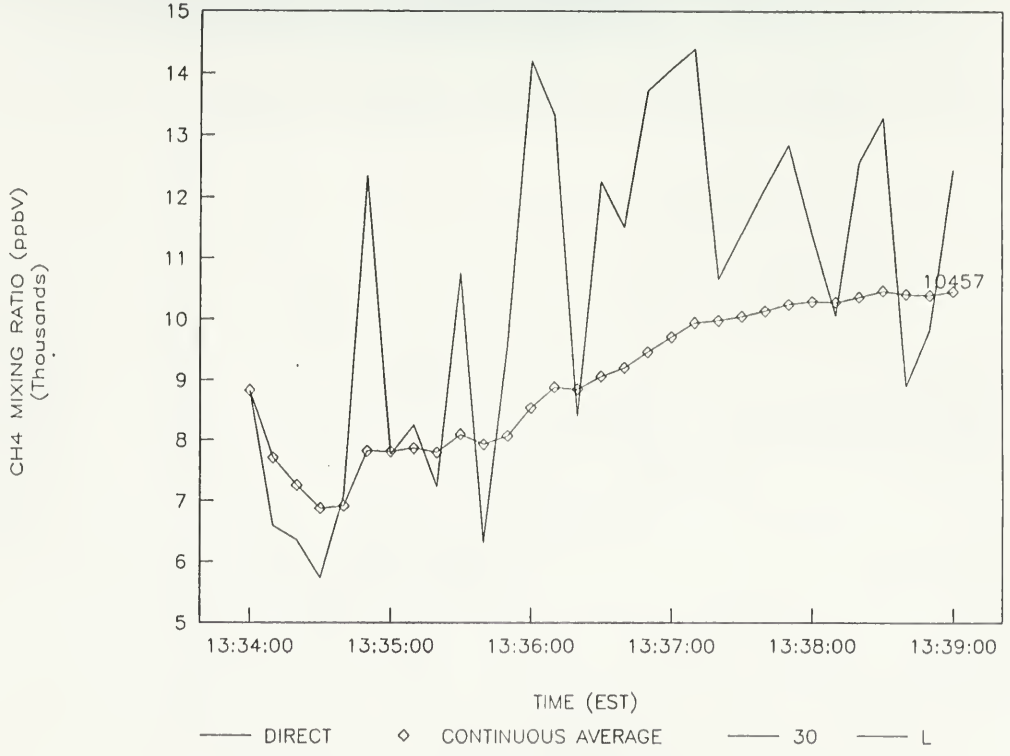
DATE : OCTOBER 12, 1994

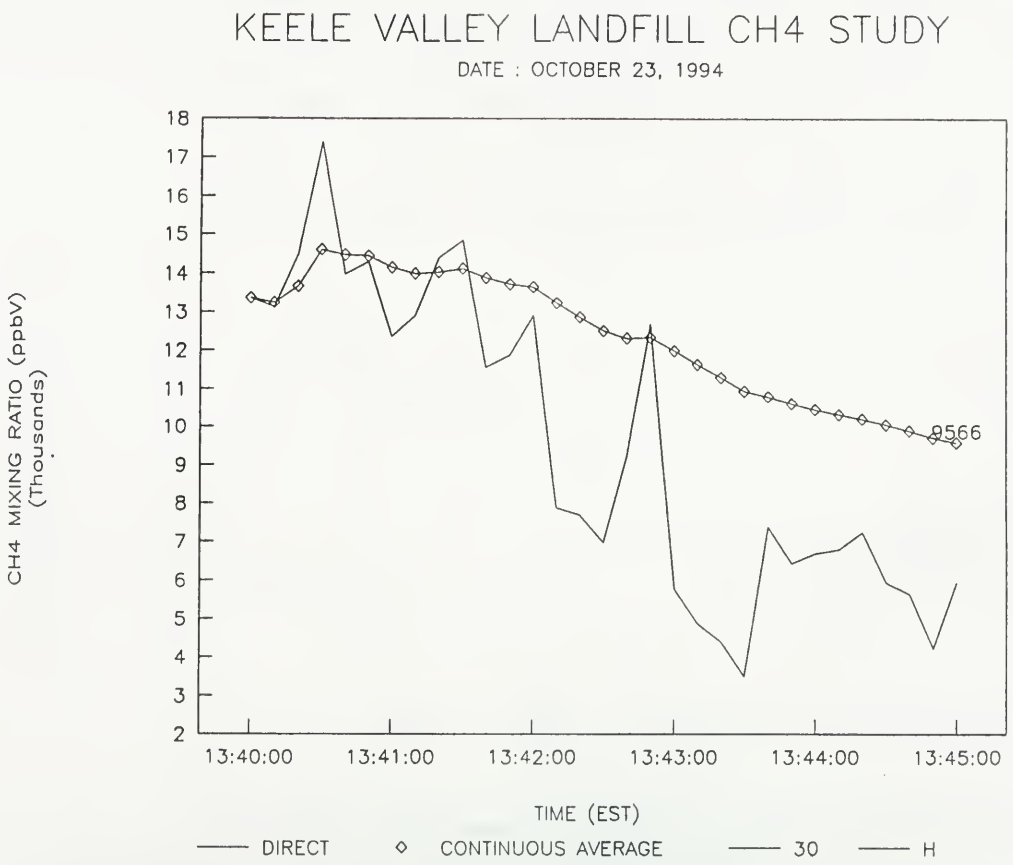



KEELE VALLEY LANDFILL CH4 STUDY
DATE : OCTOBER 12, 1994
CH4 MIXING RATIO (ppbV)
(Thousands)
2.4
2.3
2.2
2.1
2
1.9
1.8
1.7
1855
15:41:00
15:42:00
15:43:00
15:44:00
15:45:00
15:46:00
TIME (EST)
DIRECT
CONTINUOUS AVERAGE
30
H

# KEELE VALLEY LANDFILL CH4 STUDY

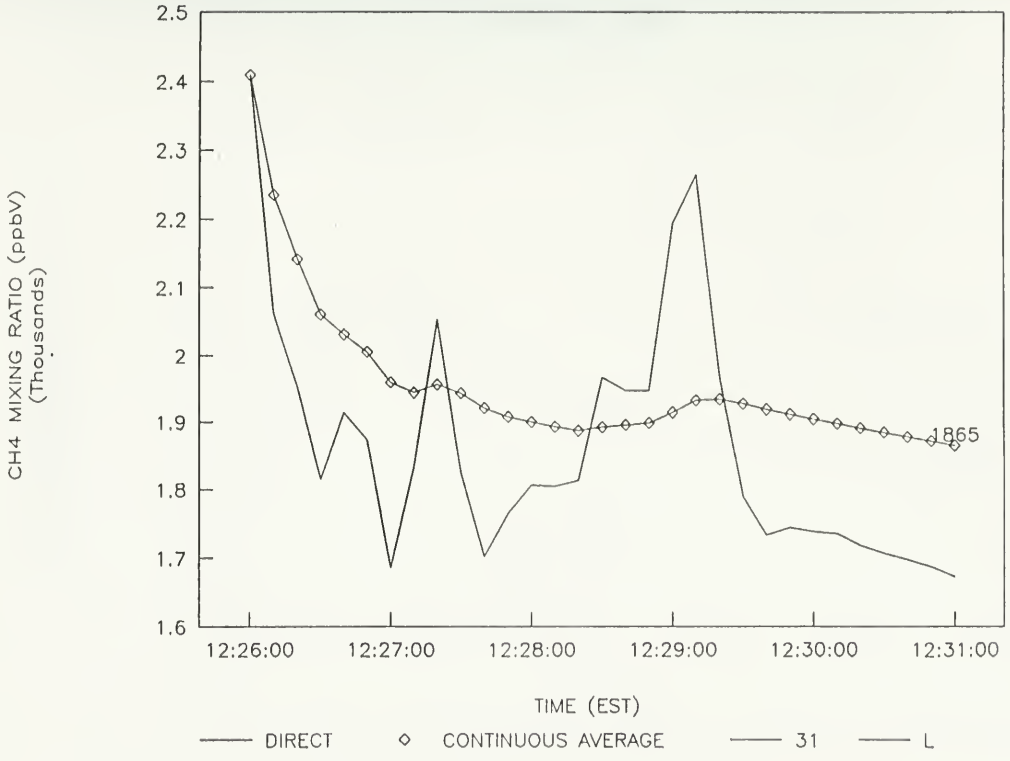
DATE : OCTOBER 23, 1994




KEELE VALLEY LANDFILL CH4 STUDY
DATE : OCTOBER 23, 1994
CH4 MIXING RATIO (ppbV)
(Thousands)
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
9566
13:40:00
13:41:00
13:42:00
13:43:00
13:44:00
13:45:00
TIME (EST)
DIRECT
CONTINUOUS AVERAGE
30
H

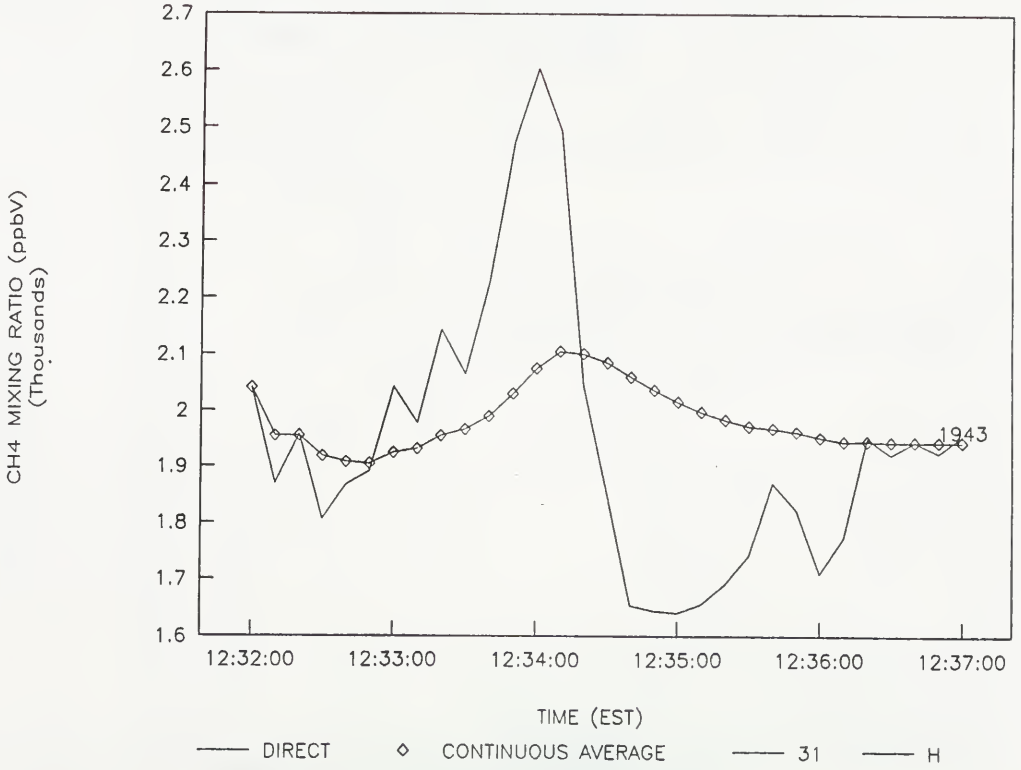
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



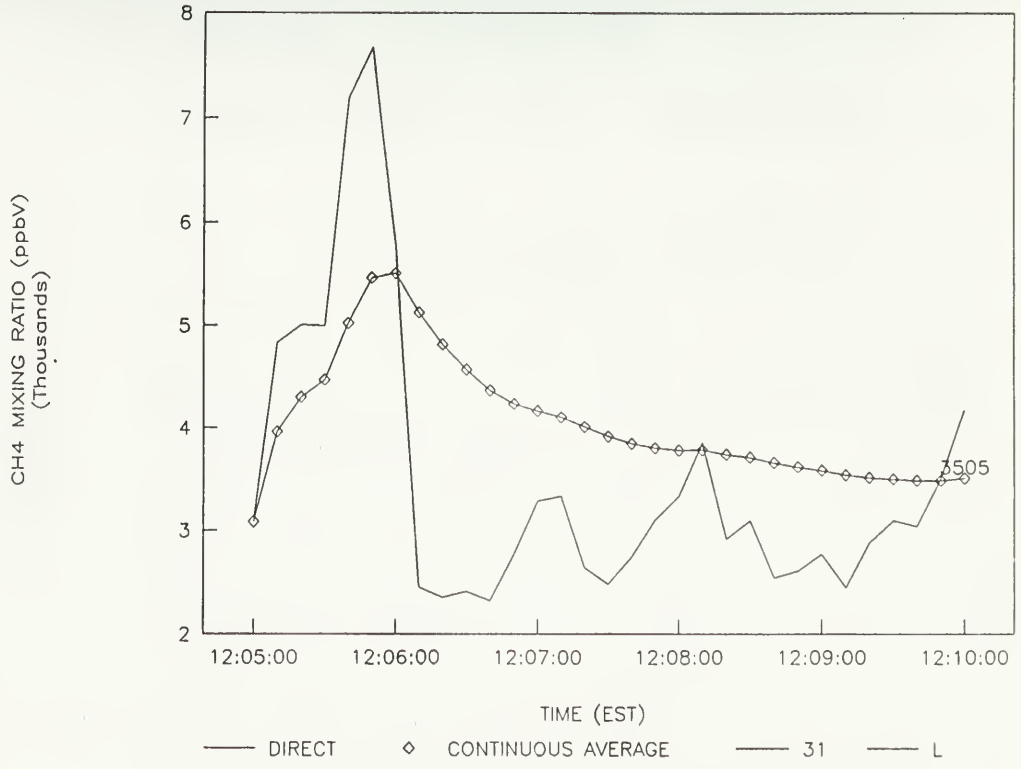
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



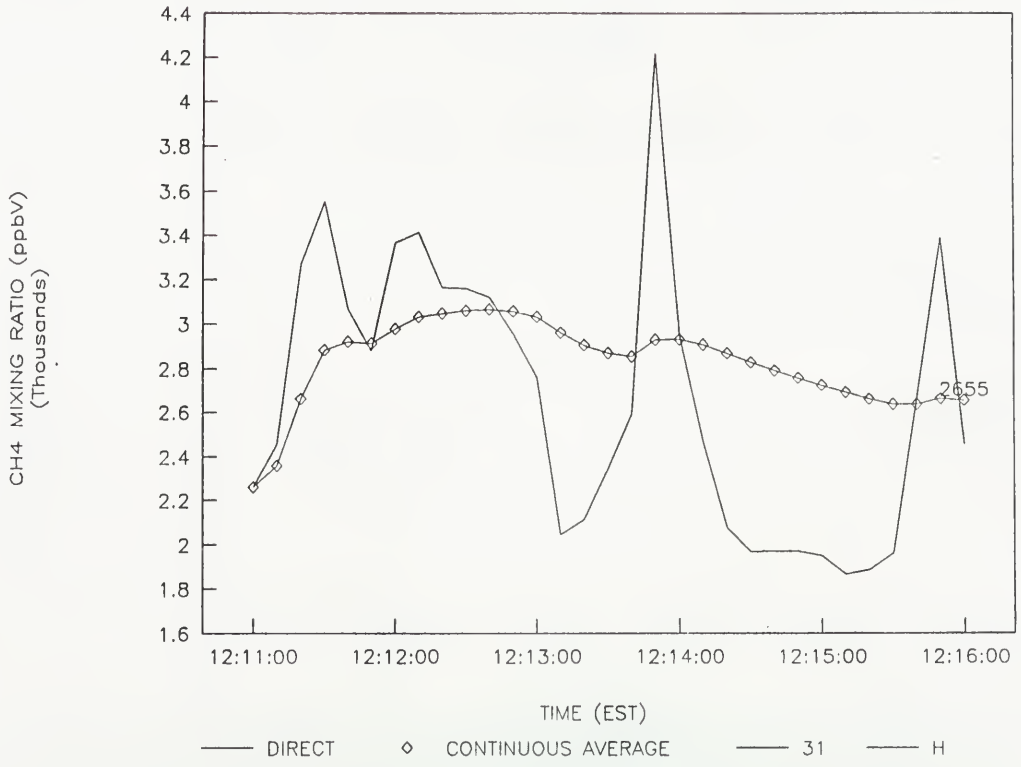
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



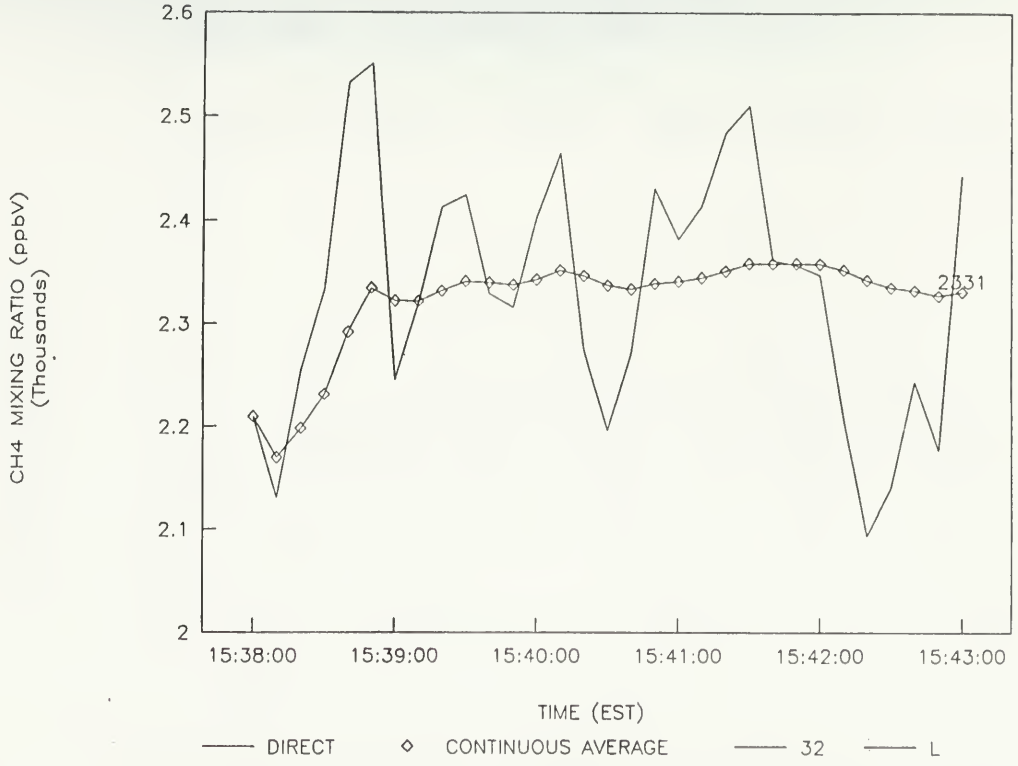
# KEELE VALLEY LANDFILL CH4 STUDY

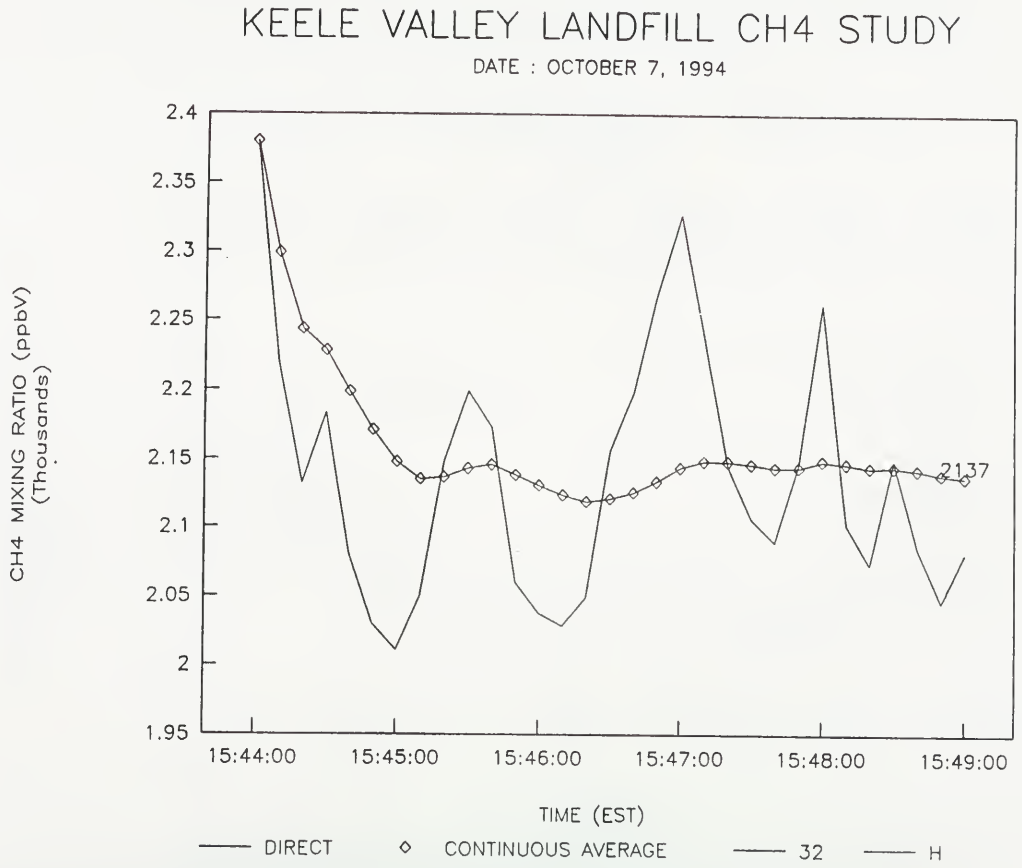
DATE : OCTOBER 12, 1994



# KEELE VALLEY LANDFILL CH4 STUDY

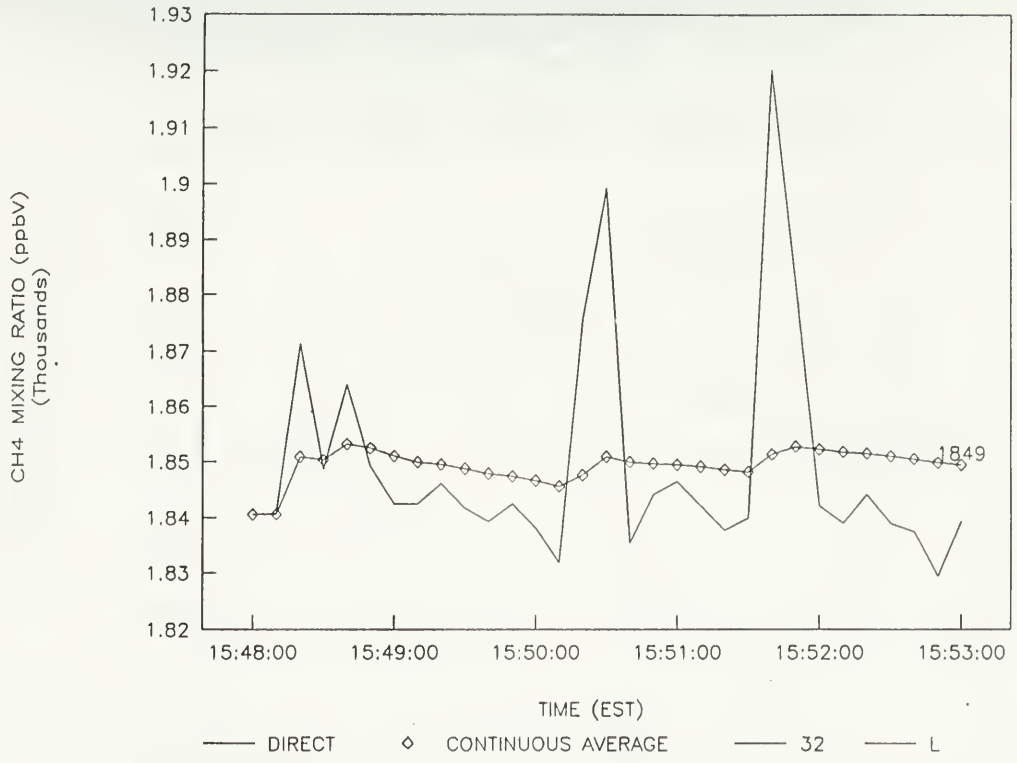
DATE : OCTOBER 7, 1994

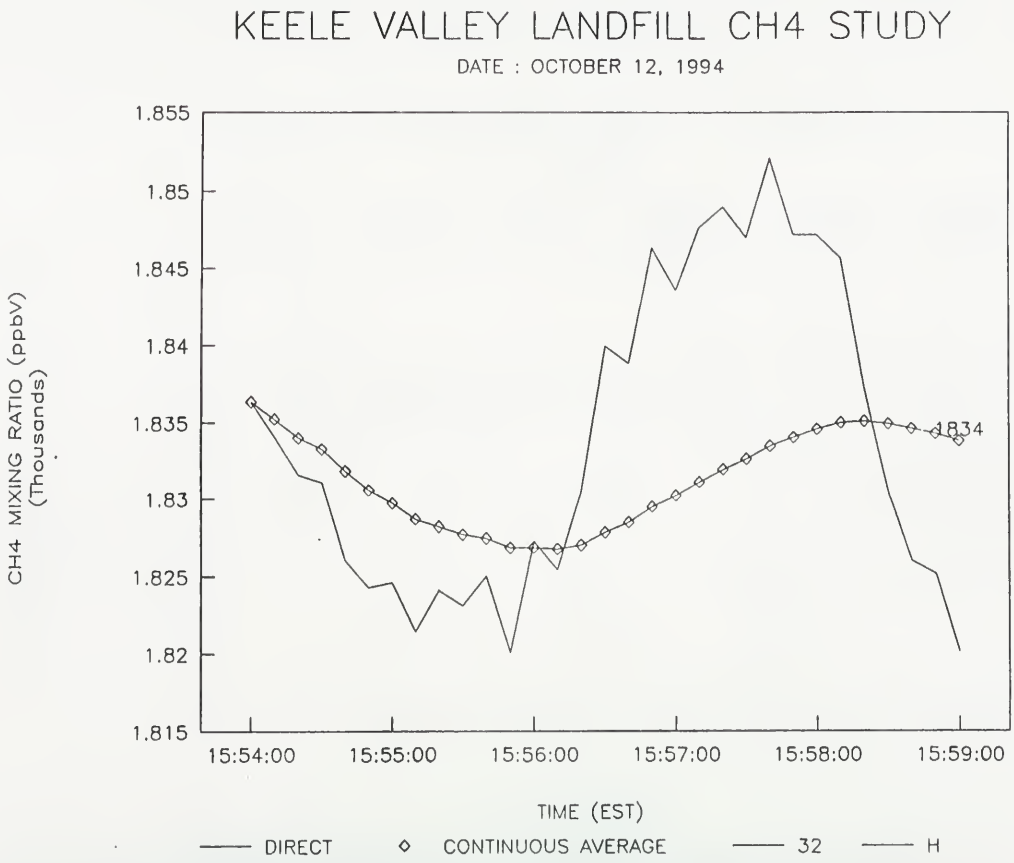



KEELE VALLEY LANDFILL CH4 STUDY
DATE : OCTOBER 7, 1994
CH4 MIXING RATIO (ppbV)
(Thousands)
2.4
2.35
2.3
2.25
2.2
2.15
2.1
2.05
2
1.95
2137
15:44:00
15:45:00
15:46:00
15:47:00
15:48:00
15:49:00
TIME (EST)
DIRECT
CONTINUOUS AVERAGE
32
H

# KEELE VALLEY LANDFILL CH4 STUDY

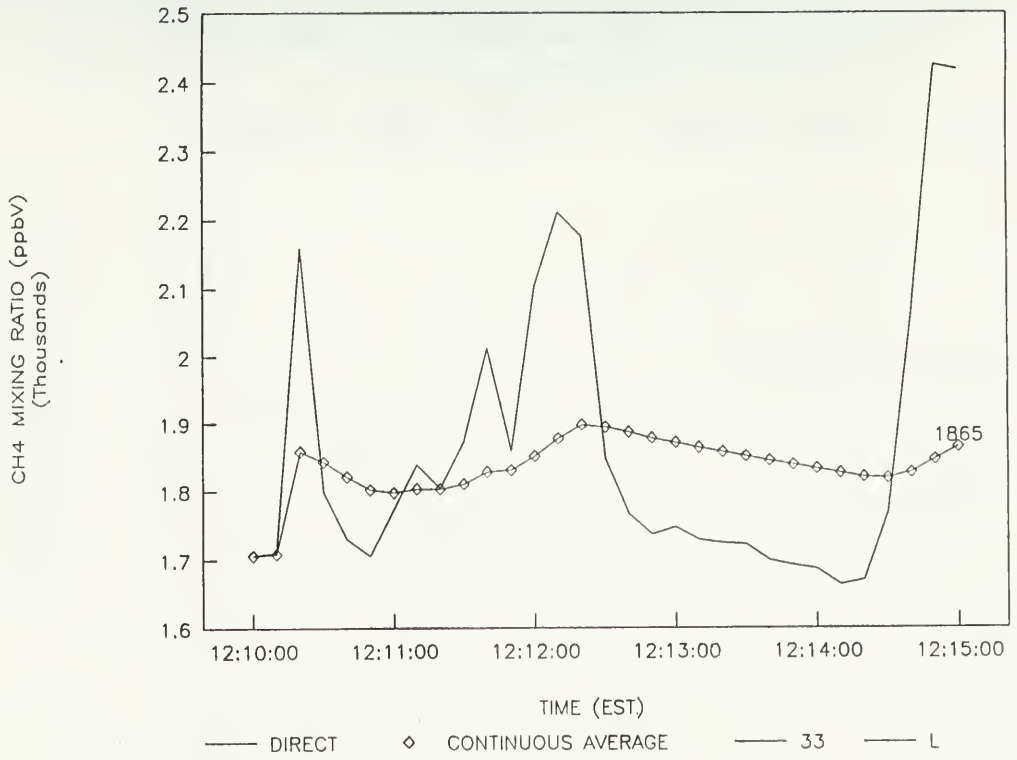
DATE : OCTOBER 12, 1994




KEELE VALLEY LANDFILL CH4 STUDY
DATE : OCTOBER 12, 1994
CH4 MIXING RATIO (ppbV)
(Thousands)
1.855
1.85
1.845
1.84
1.835
1.83
1.825
1.82
1.815
1834
15:54:00
15:55:00
15:56:00
15:57:00
15:58:00
15:59:00
TIME (EST)
DIRECT
CONTINUOUS AVERAGE
32
H

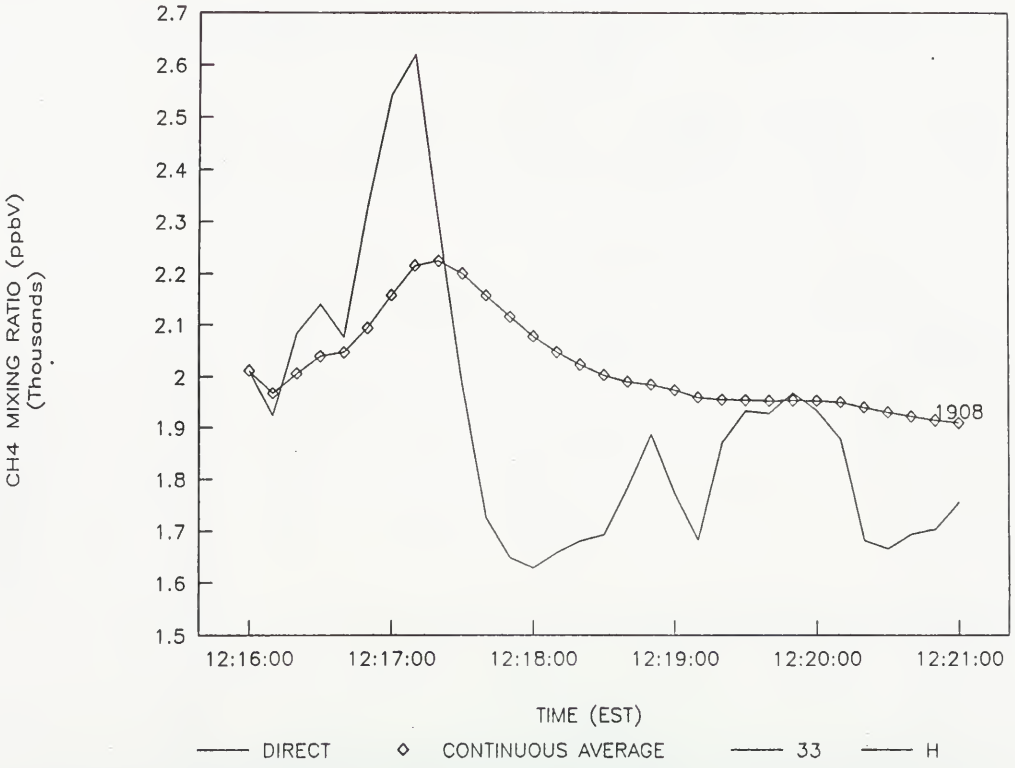
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



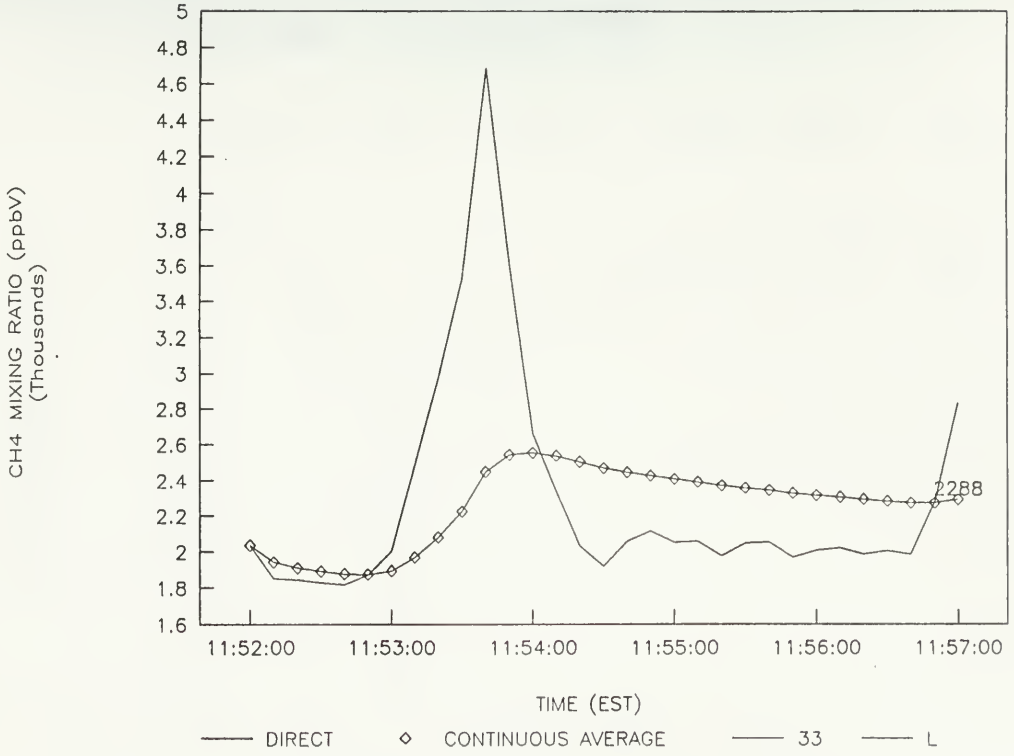
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 6, 1994



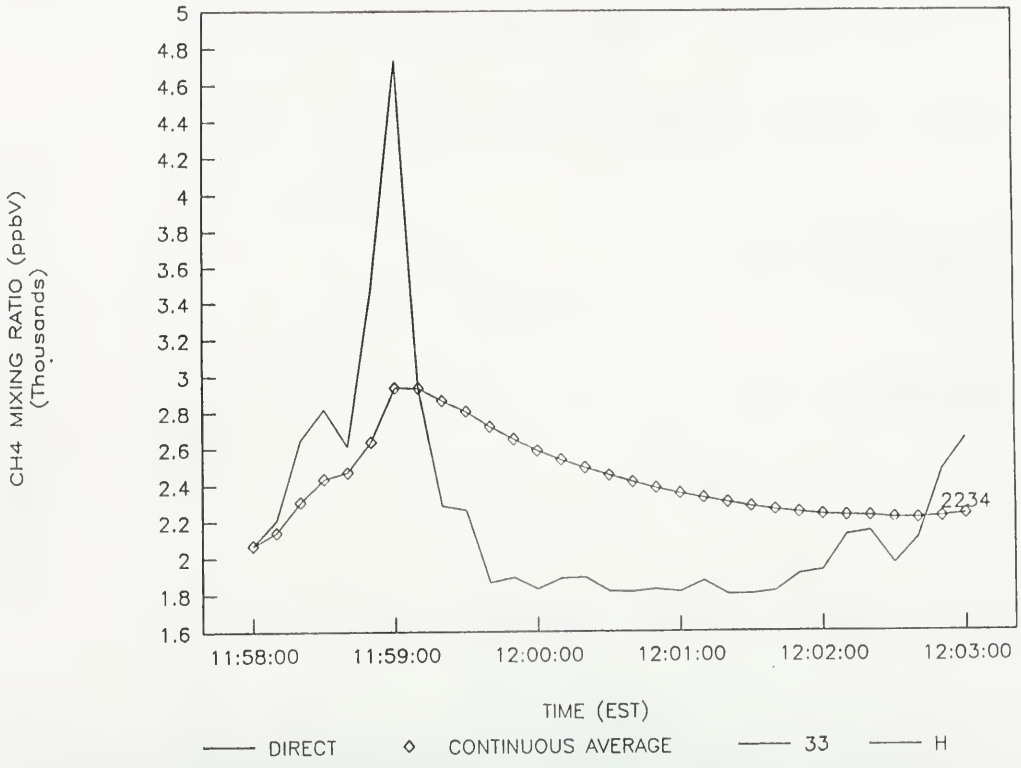
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



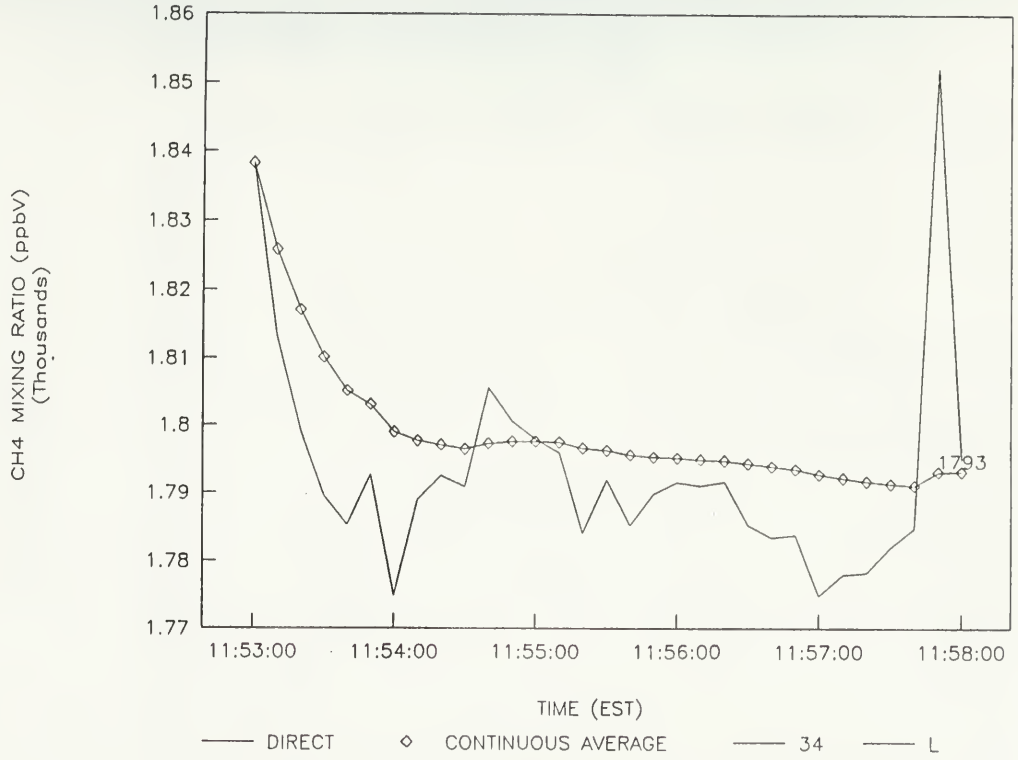
# KEELE VALLEY LANDFILL CH4 STUDY

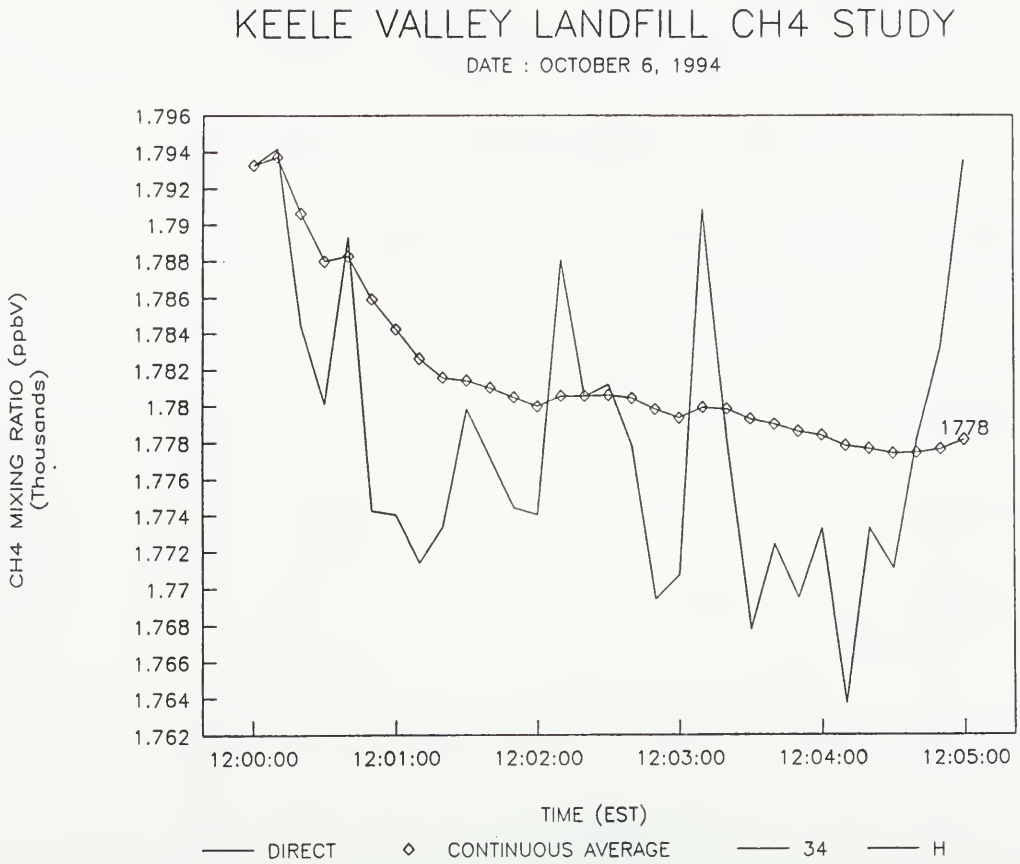
DATE : OCTOBER 12, 1994



# KEELE VALLEY LANDFILL CH4 STUDY

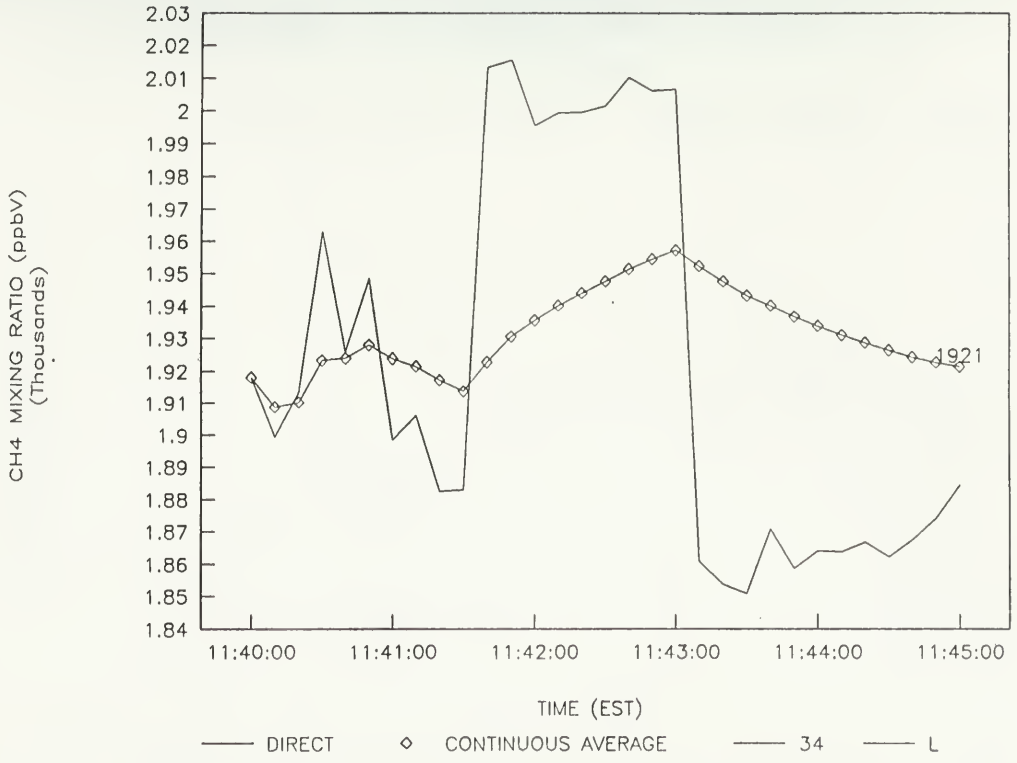
DATE : OCTOBER 6, 1994




KEELE VALLEY LANDFILL CH4 STUDY
DATE : OCTOBER 6, 1994
CH4 MIXING RATIO (ppbV)
(Thousands)
1.796
1.794
1.792
1.79
1.788
1.786
1.784
1.782
1.78
1.778
1.776
1.774
1.772
1.77
1.768
1.766
1.764
1.762
1778
12:00:00
12:01:00
12:02:00
12:03:00
12:04:00
12:05:00
TIME (EST)
DIRECT
CONTINUOUS AVERAGE
34
H

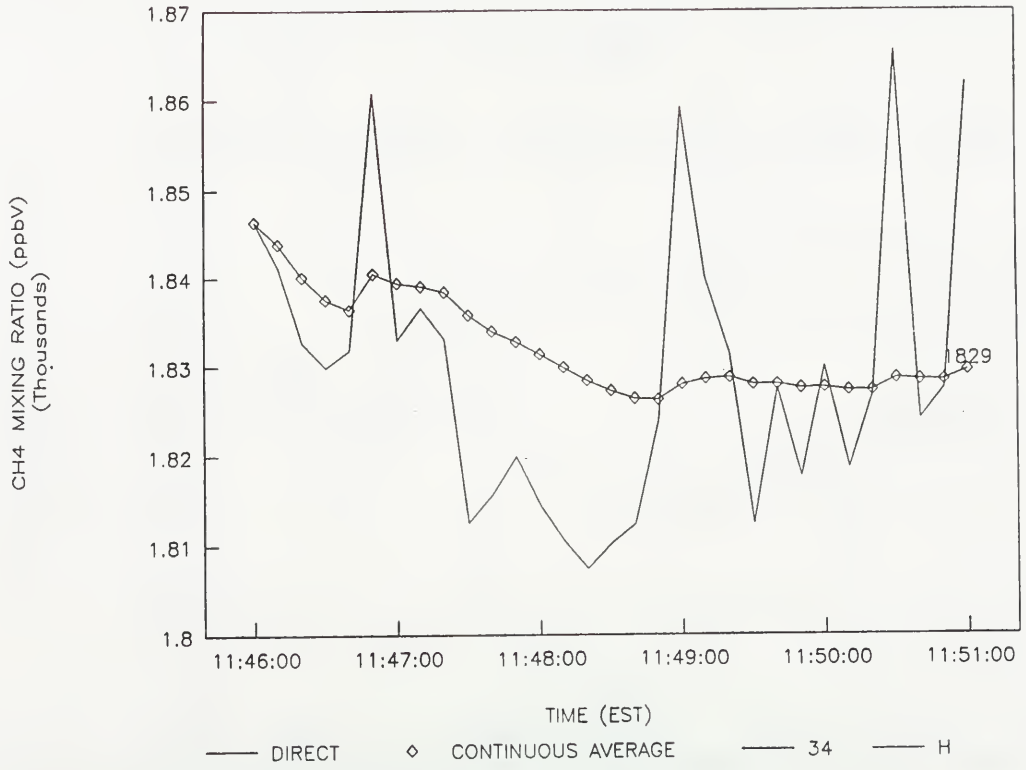
# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



# KEELE VALLEY LANDFILL CH4 STUDY

DATE : OCTOBER 12, 1994



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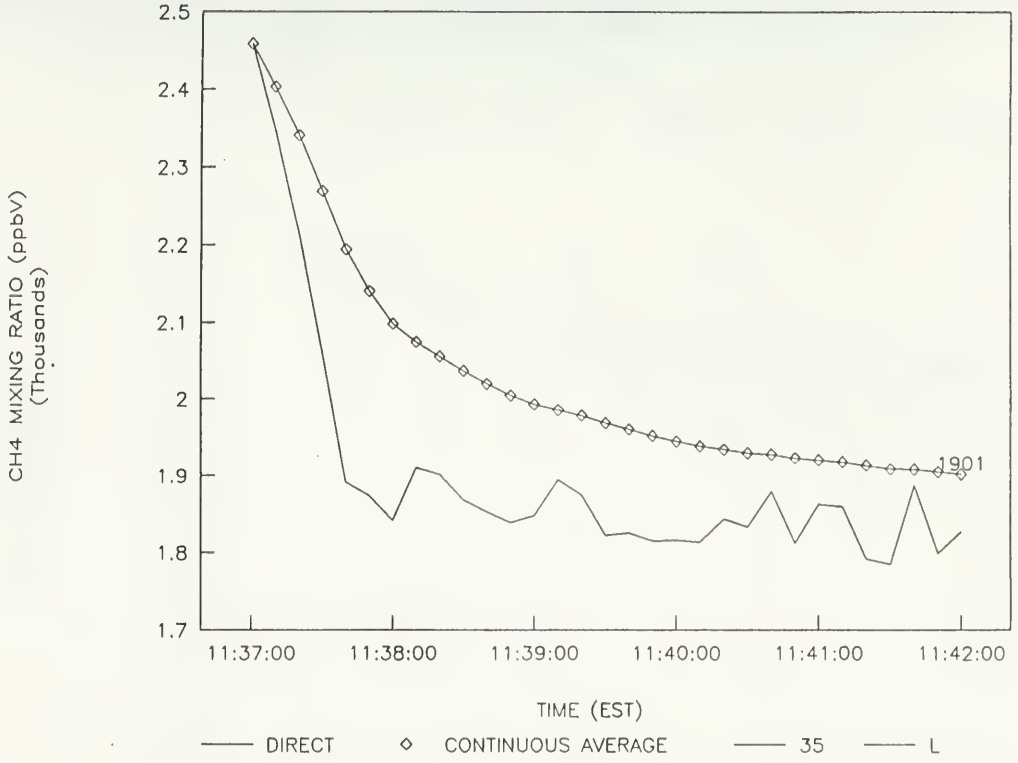

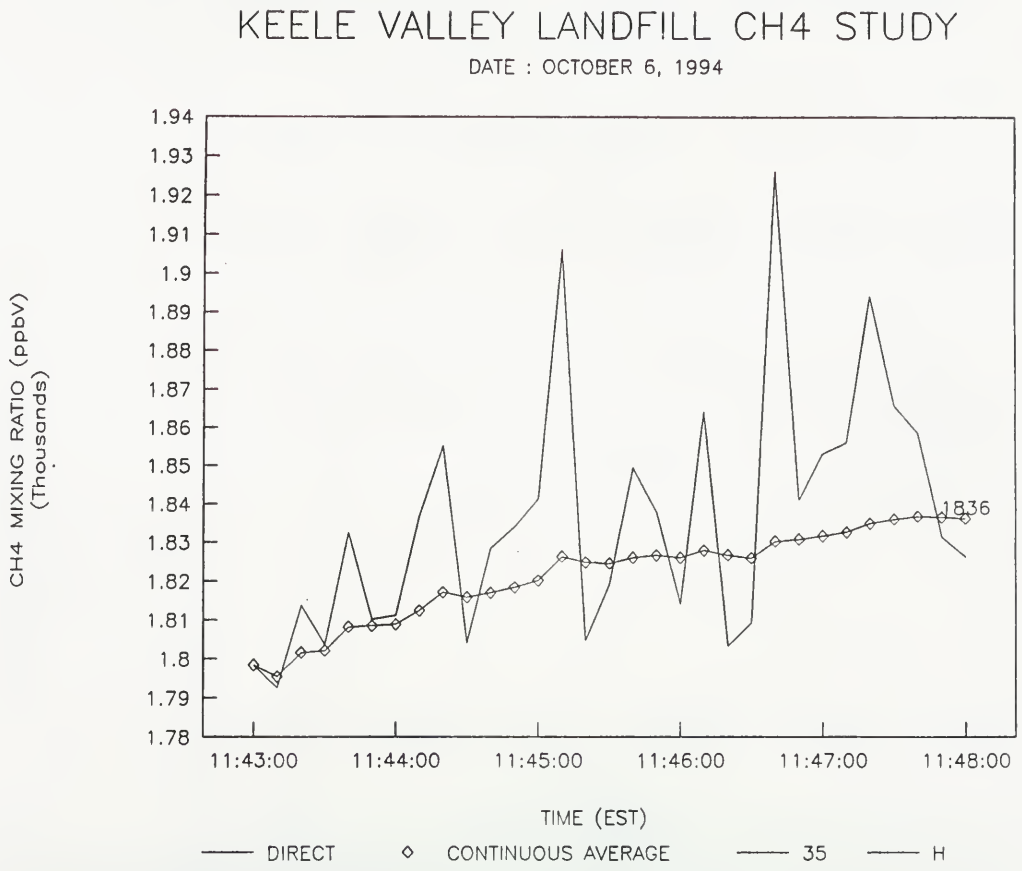
KEELE VALLEY LANDFILL CH4 STUDY
DATE : OCTOBER 6, 1994
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(Thousands)
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1.91
1.9
1.89
1.88
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1.79
1.78
1836
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TIME (EST)
DIRECT
CONTINUOUS AVERAGE
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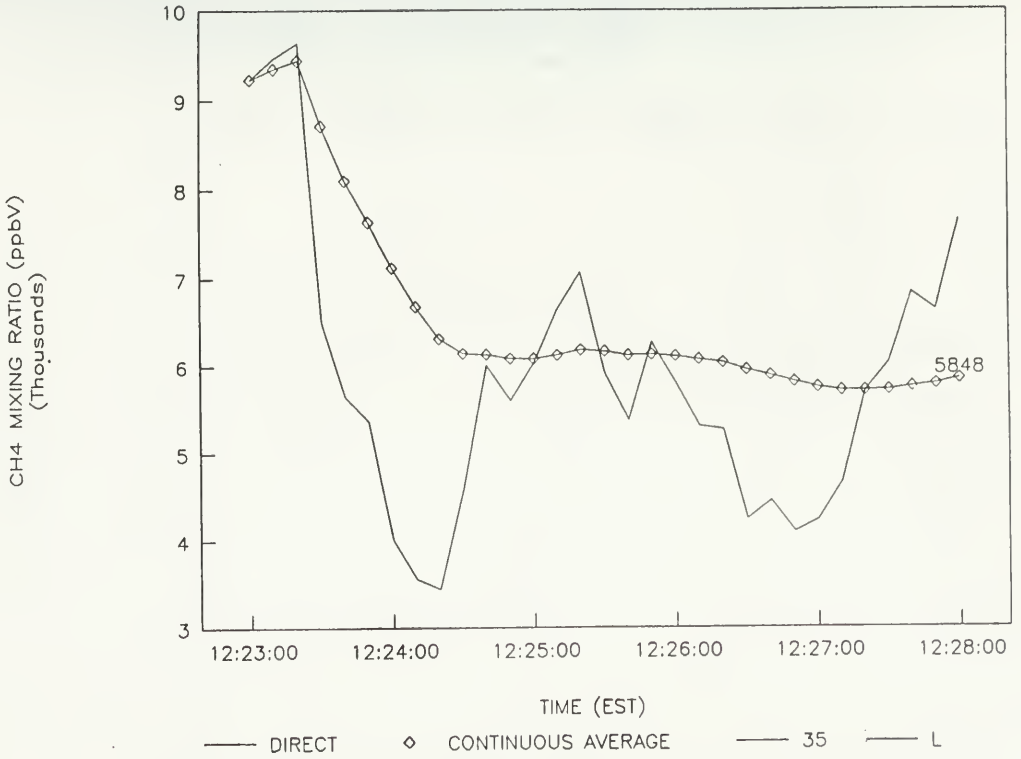
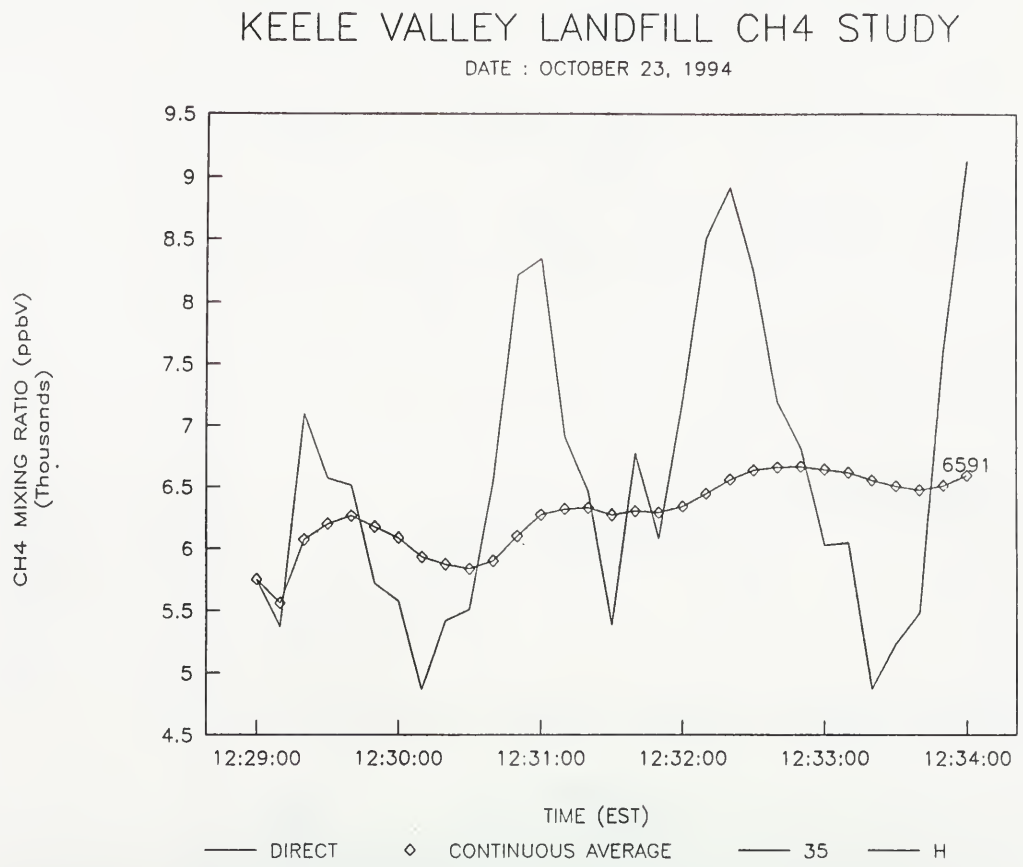
DATE : OCTOBER 23, 1994




KEELE VALLEY LANDFILL CH4 STUDY
DATE : OCTOBER 23, 1994
CH4 MIXING RATIO (ppbV)
(Thousands)
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7.5
7
6.5
6
5.5
5
4.5
6591
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TIME (EST)
DIRECT
CONTINUOUS AVERAGE
35
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# KEELE VALLEY LANDFILL CH4 STUDY

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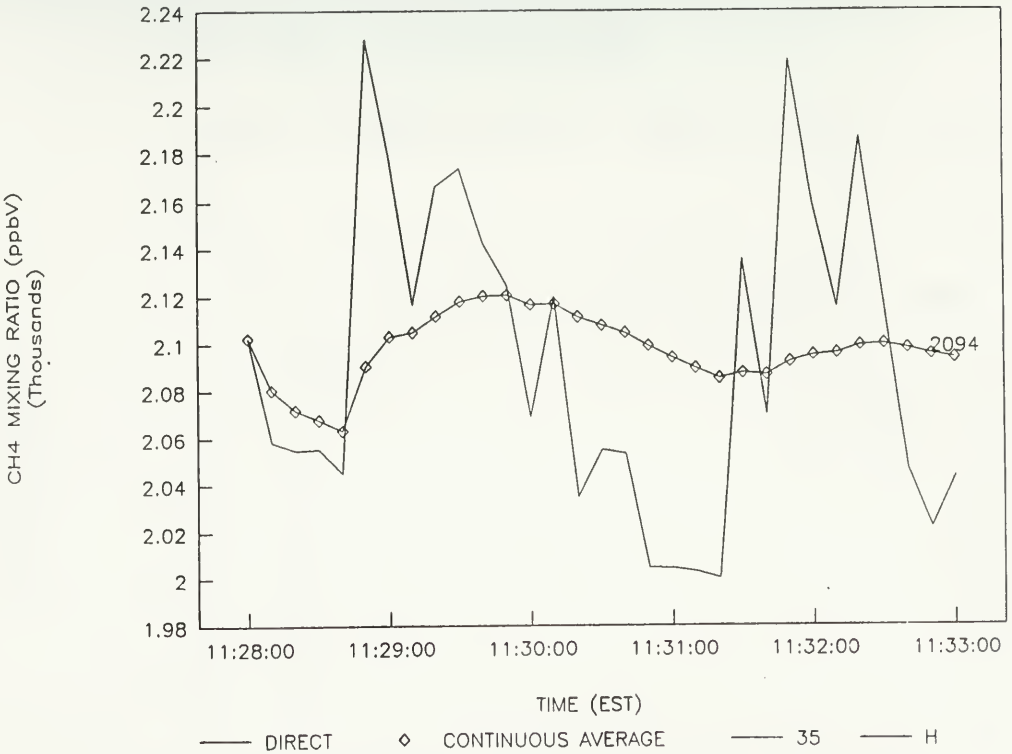

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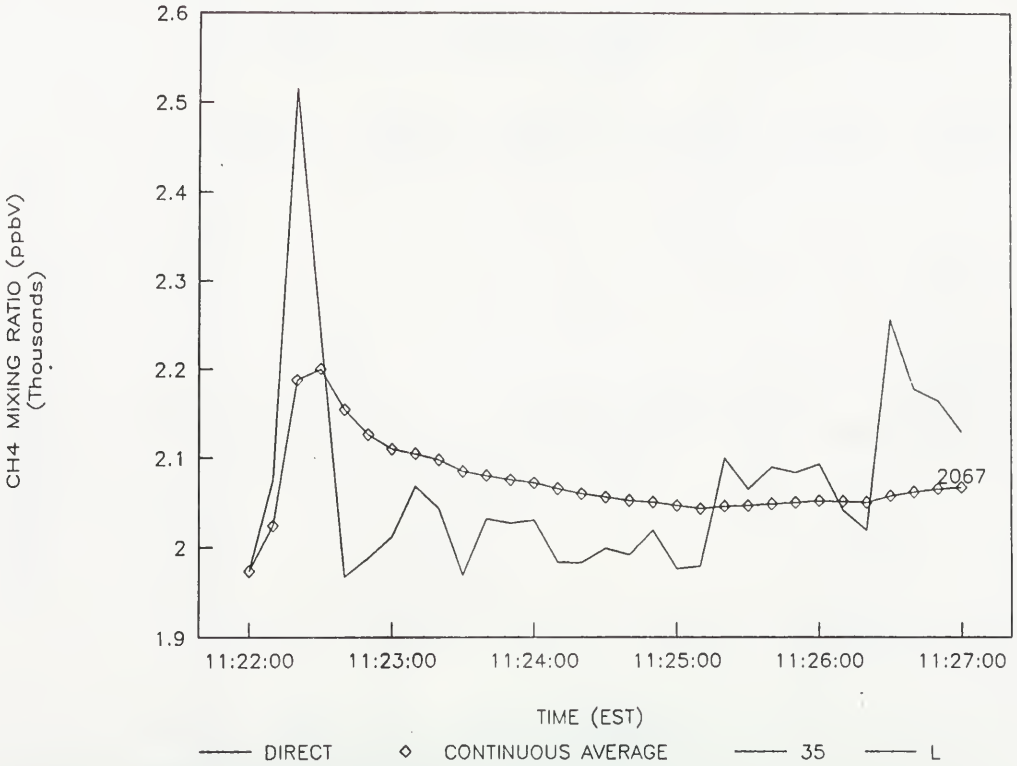

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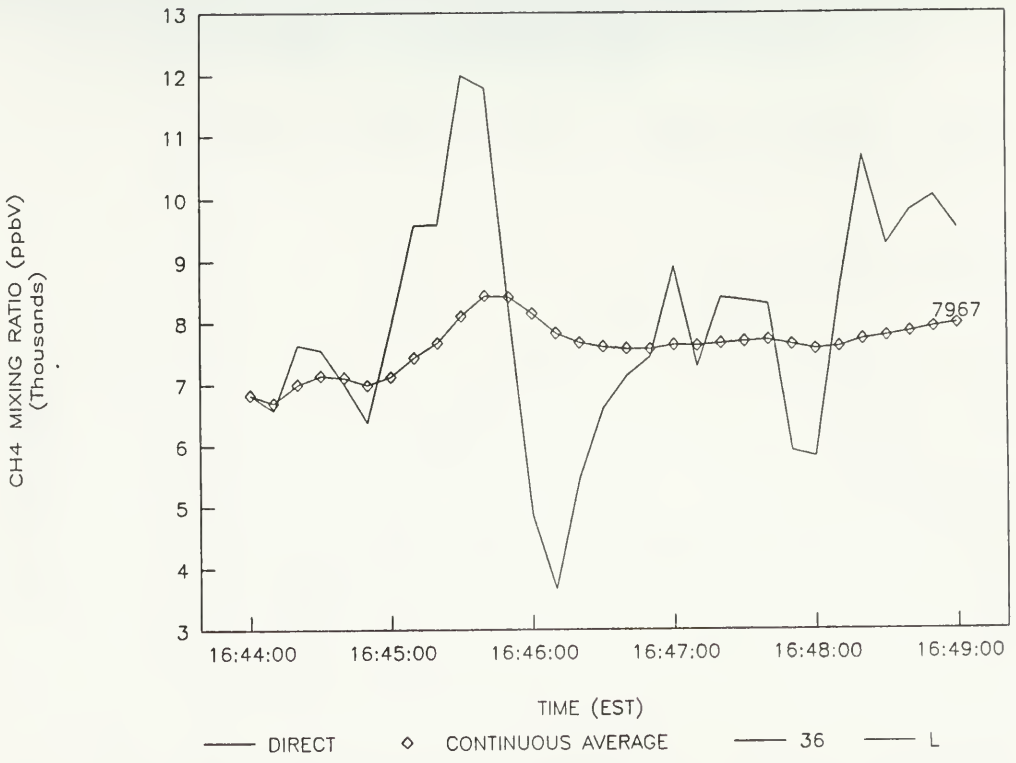

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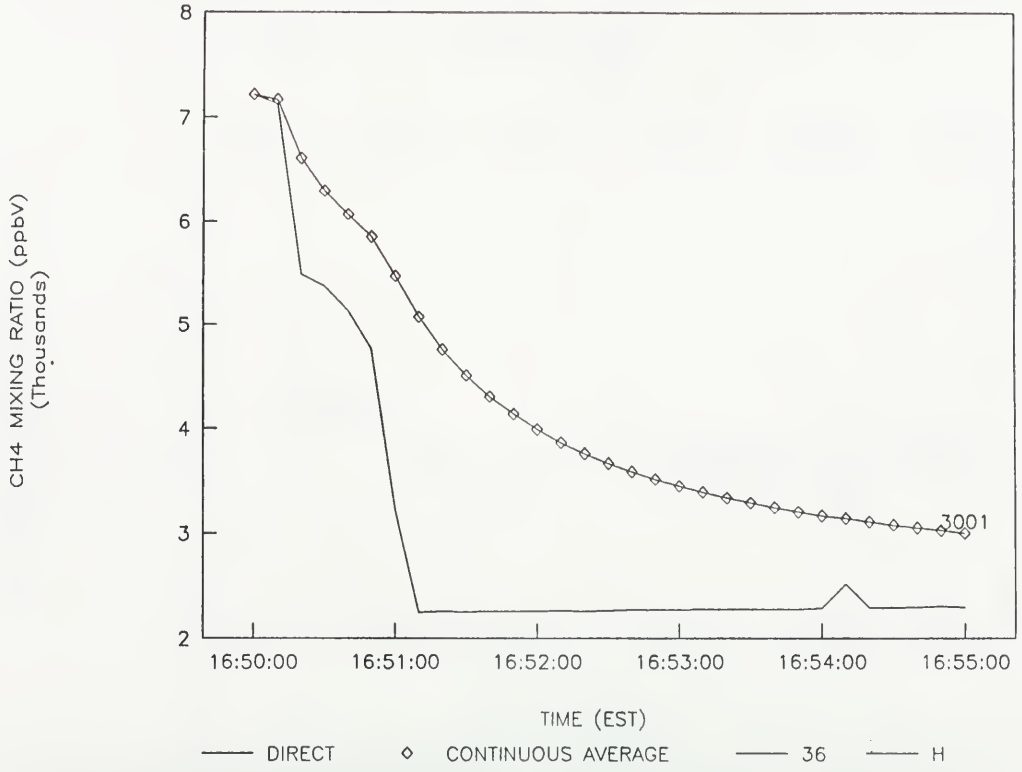

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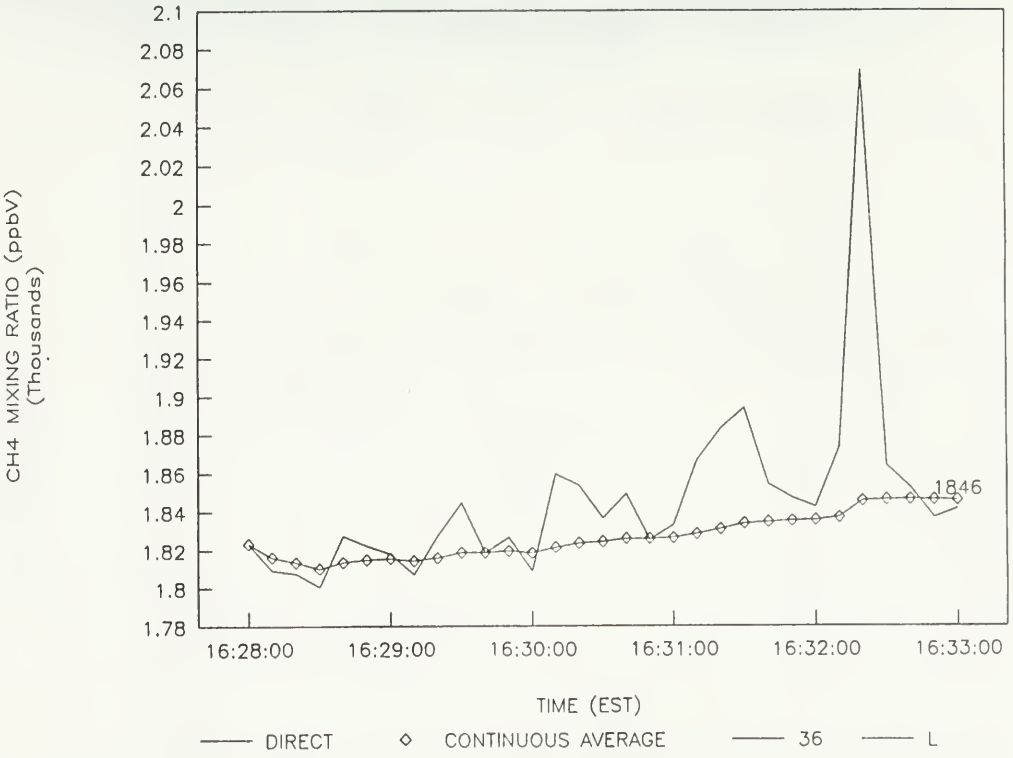

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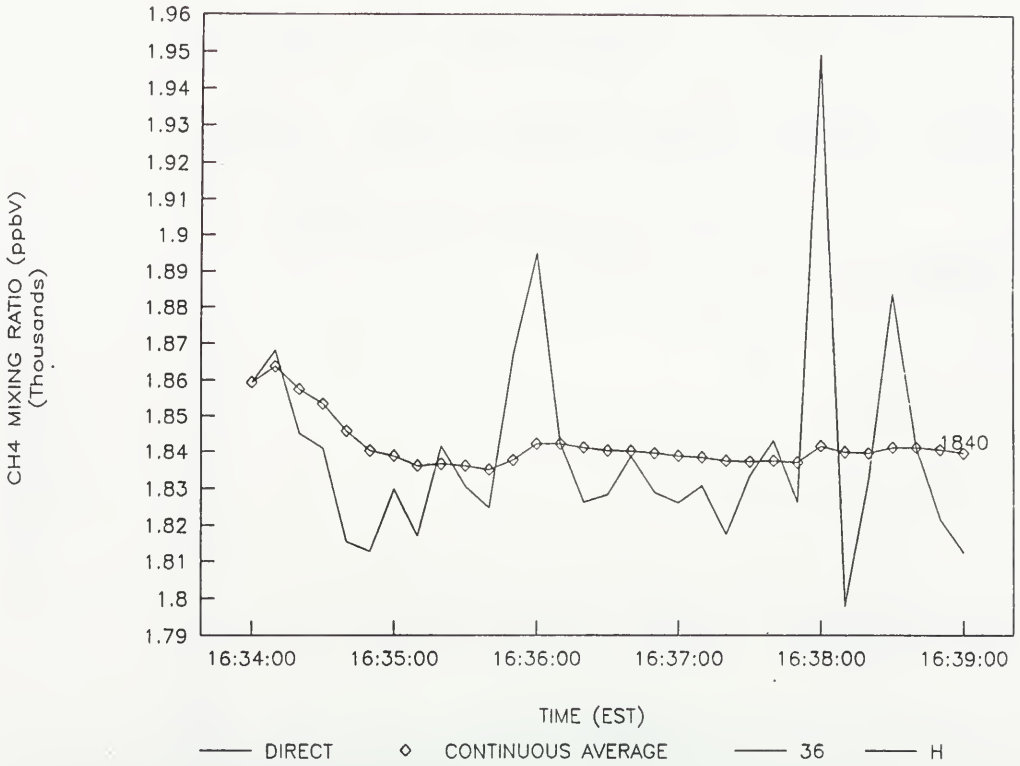

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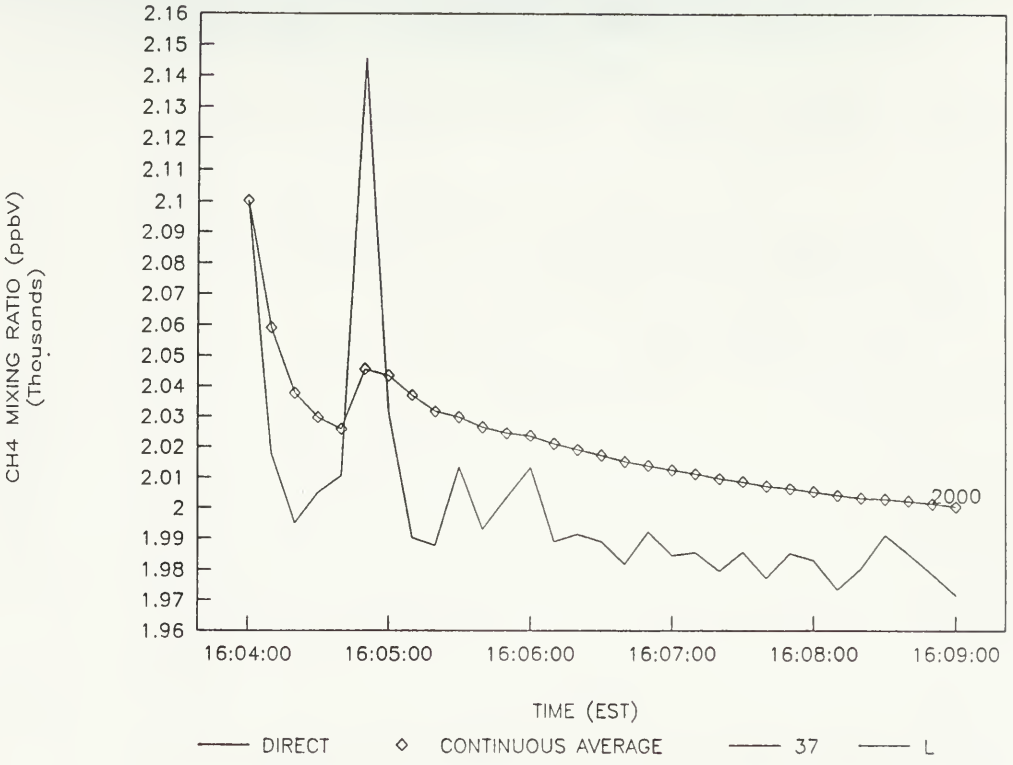
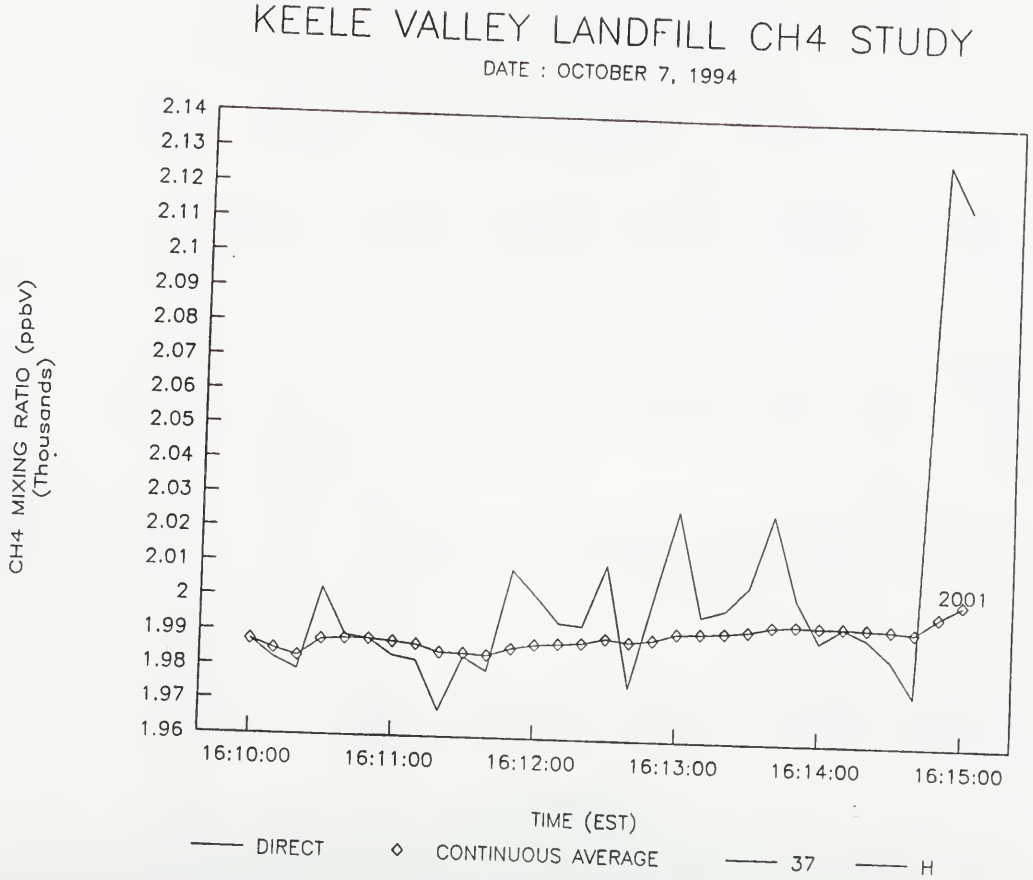
DATE : OCTOBER 7, 1994




KEELE VALLEY LANDFILL CH4 STUDY
DATE : OCTOBER 7, 1994
CH4 MIXING RATIO (ppbV)
(Thousands)
2.14
2.13
2.12
2.11
2.1
2.09
2.08
2.07
2.06
2.05
2.04
2.03
2.02
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TIME (EST)
DIRECT
CONTINUOUS AVERAGE
37
H

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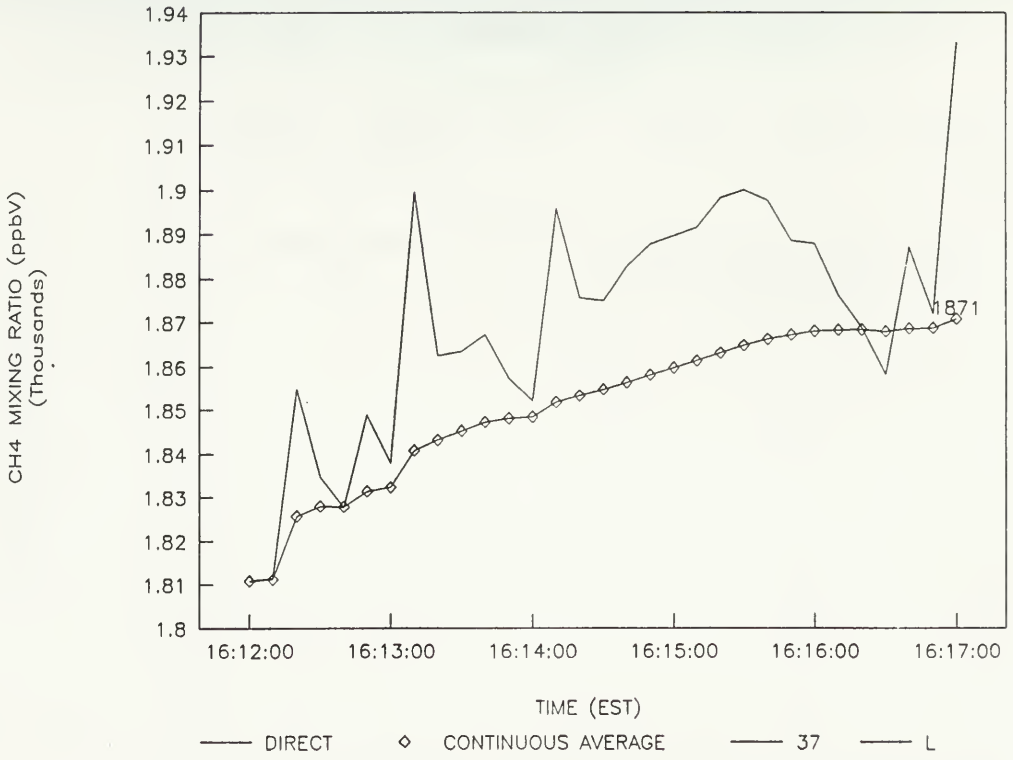
DATE : OCTOBER 12, 1994



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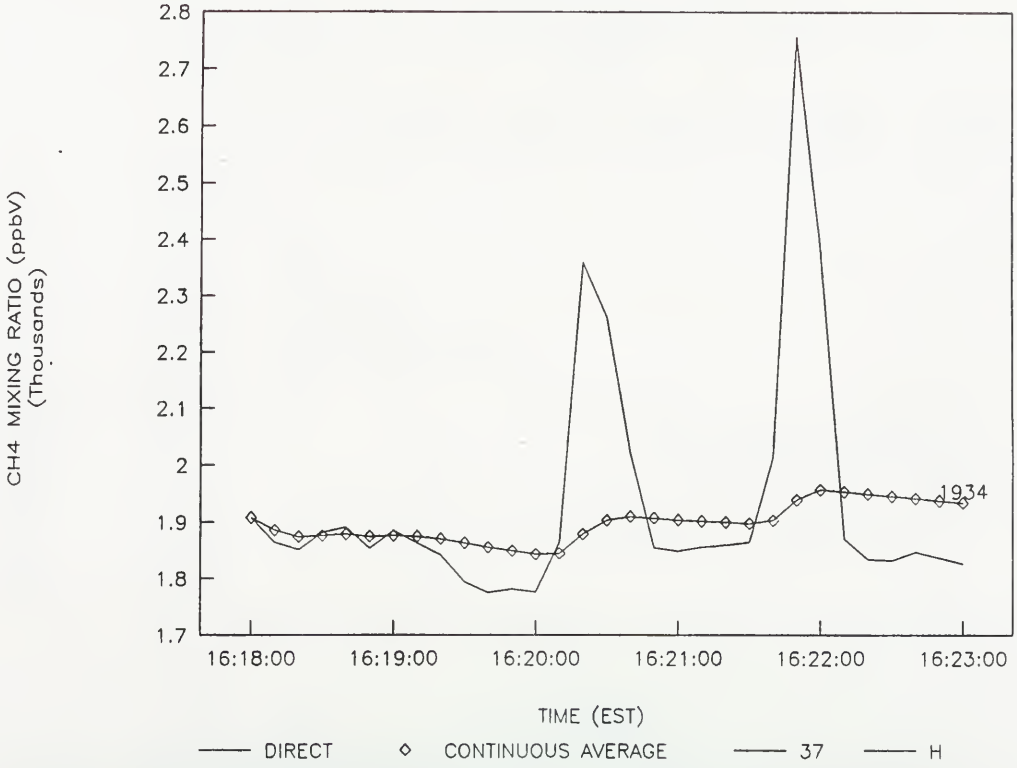

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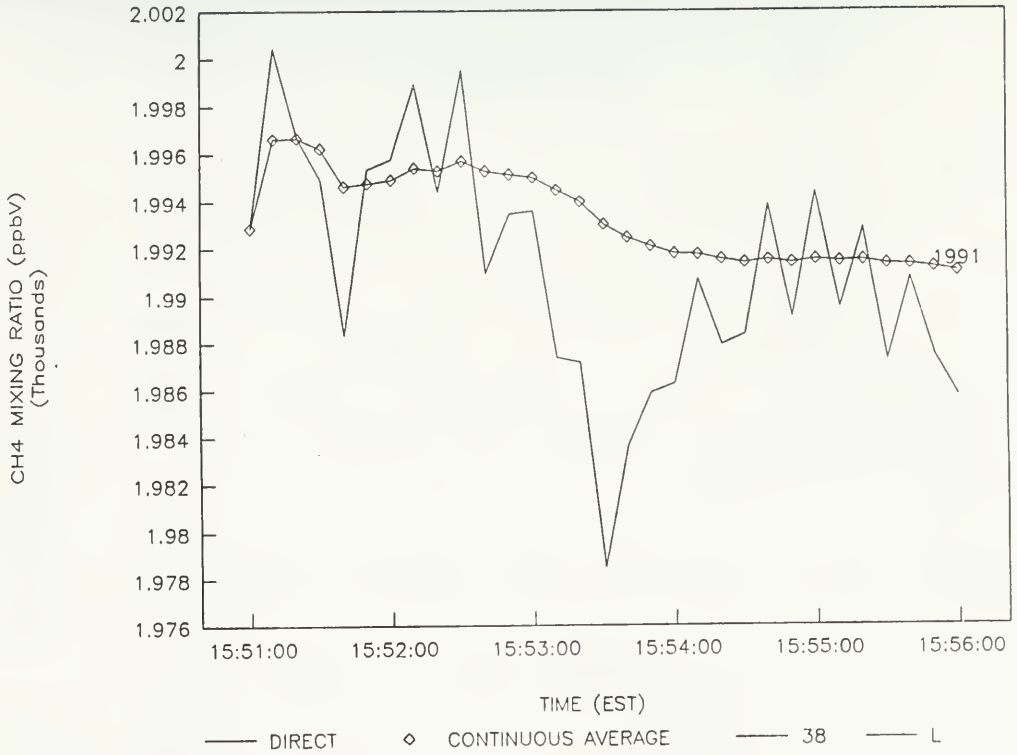

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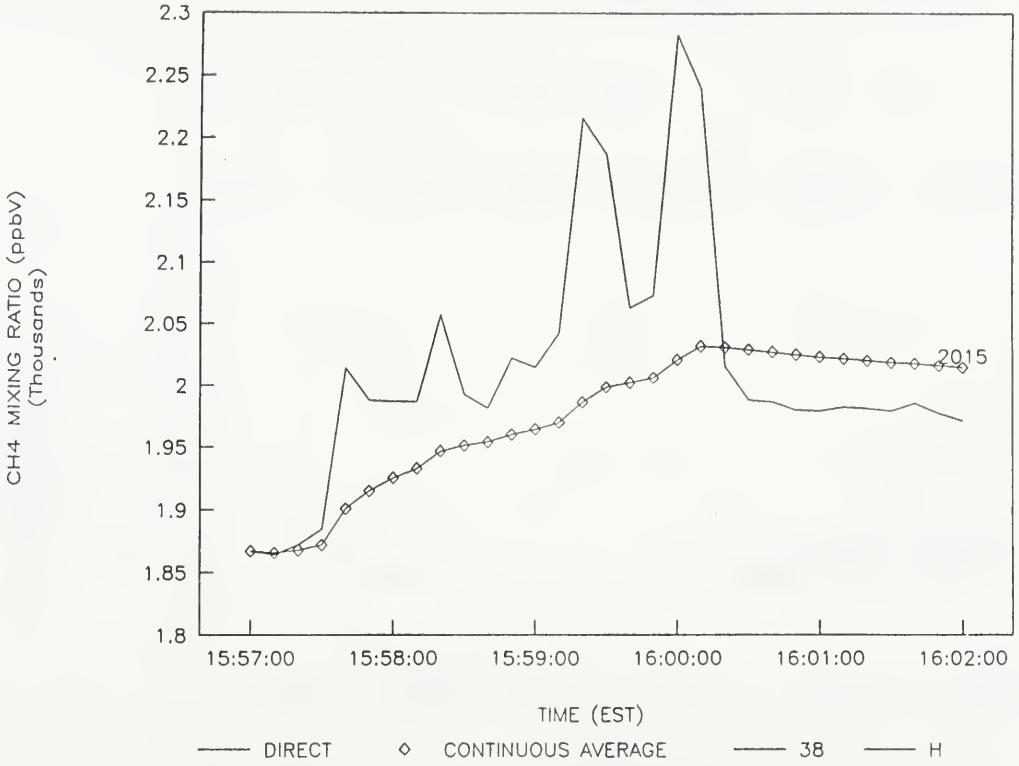

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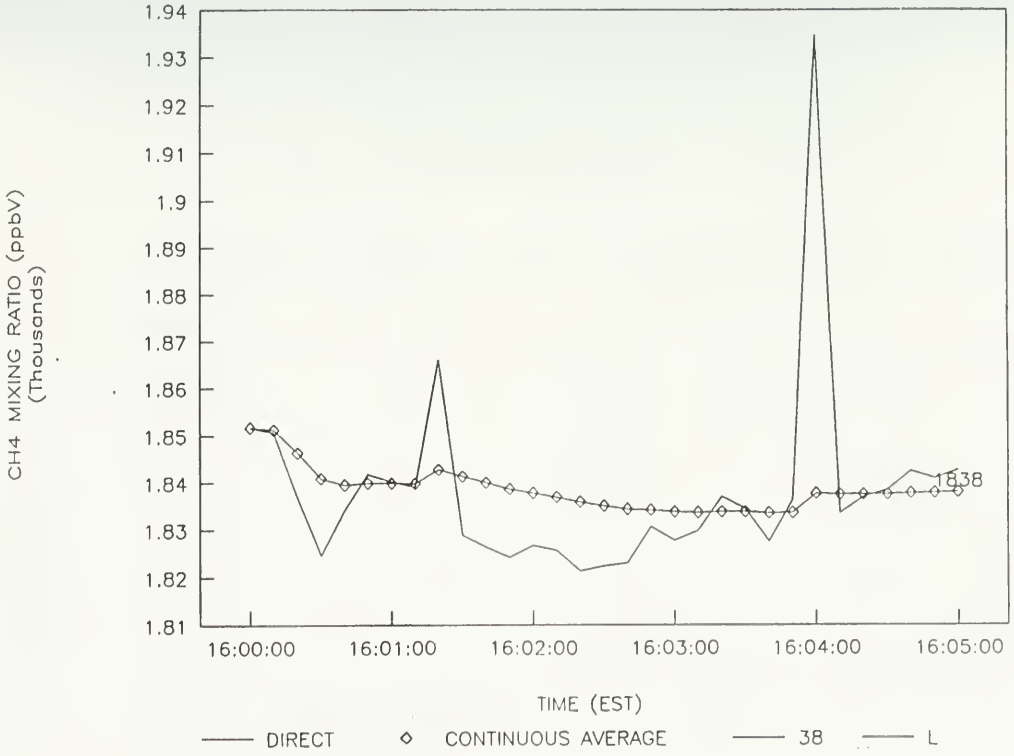

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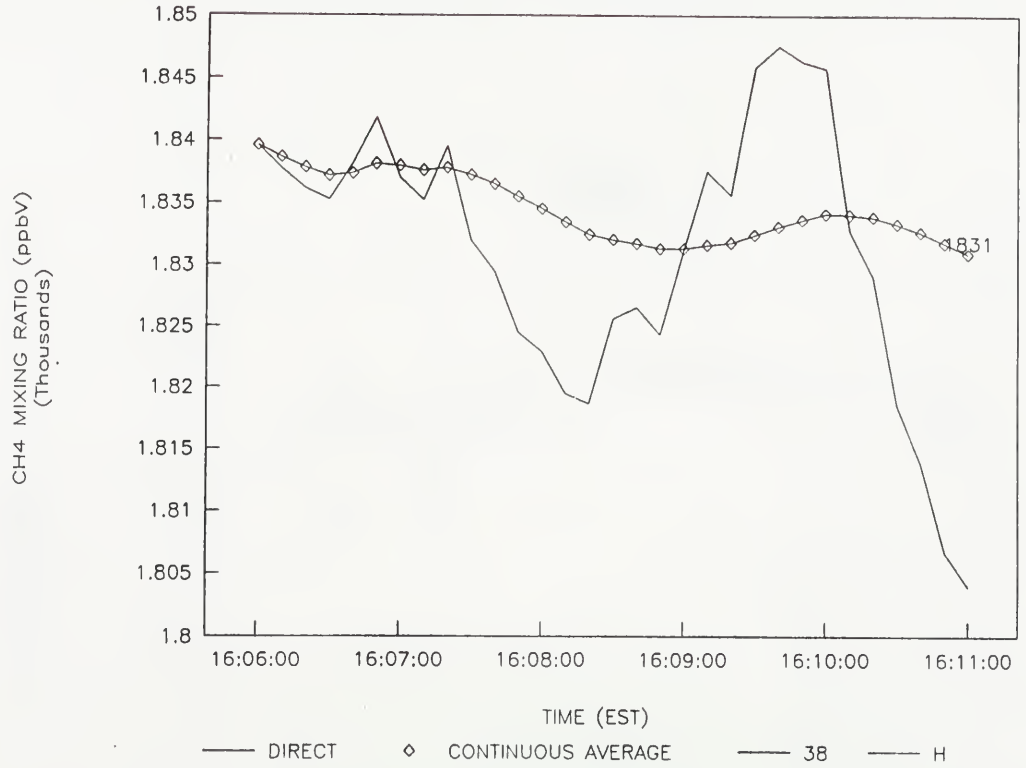

# APPENDIX B

# THE LASAIR - NEW REMOTE SENSING INSTRUMENTS BASED ON NEAR INFRARED DIODE LASERS

H. I. Schiff, S. D. Nadler and G. I. Mackay

UNISEARCH ASSOCIATES INC., 222 Snidercroft Road, Concord, Ontario, L4K 1B5, CANADA

## ABSTRACT

Three versions of a near infrared system based on commercial communication type laser diodes have been developed. They have high selectivity and good sensitivity for a number of important gases. All three systems use a common control and data logging and analysis box. The LASAIR-R is a simple, inexpensive, remote sensing instrument using a single 10 cm Cassegrain telescope to both transmit and receive the laser beam. The LASAIR-S is a system for continuous, non-extractive stack monitoring. Fibre optics are used to take the laser beam from the control box (suitably located in the plant), to the stack and to bring the return back to the box. The LASAIR-P is a point source instrument using a multipath cell inside the box to provide the sensitivity required. The ease of operation and the relatively low cost should make these systems an attractive method for measuring specific gases for industrial and regulatory markets.

## 1. INTRODUCTION

Tunable Diode Laser Absorption Spectroscopy (TDLAS) operating in the mid infrared spectral region is the best method available for making air measurements where specificity, sensitivity and fast time response is required. With this technique it is possible to measure gases with virtually no interferences between one another, with sensitivities of parts per trillion and with time resolution of fractions of seconds. TDLAS systems have been used to make high quality measurements in a variety of environments from the pristine air over Mauna Loa to the polluted air of Los Angeles to dynamometer studies of auto exhaust. TDLAS instruments have been carried on mobile vans, ships, aircraft, balloons and even on rockets. Despite the success of this technique, the use of TDLAS for air measurements has been largely confined to the university and government research communities who have continued to push its development into the area of increasing sensitivities. The technique has not yet found wide spread applications in the industrial and regulatory communities largely because of the cost and complexity of these instruments.

There are two main reasons for industry's neglect of this powerful technique. First, the Pb salt diodes which emit radiation in the mid infrared operate at low temperatures which require relatively expensive and cumbersome cryogenic cooling. Secondly, pressure broadening of most molecules in the mid IR region is rather severe which generally requires measurements using reduced pressure in multi-path cells. This largely constricts the technique to point source measurements whereas remote sensing instruments are rapidly gaining popularity for most industrial and regulatory applications.

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Both these limitations can be overcome, however, by the use of a class of tunable diodes made of crystals containing elements such as Ga, As and P which emit laser radiation in the near infrared from about 0.78 to 2.5 microns. These diodes operate at, or near, ambient temperature which permits their widespread use in the telecommunication industry and for domestic products such as CD players and laser printers. The diodes that are used for these purposes, are of relatively high quality and power and low cost. Moreover, the ratio of pressure to Doppler broadening is generally not as severe in the near IR which permit development of remote sensing, long path instruments which can operate at atmospheric pressure.

The limitations of operating in the near IR is that relatively few molecules have absorptions in this spectral region. This may actually be an advantage for measurements of those that do since there is much less chance of mutual interferences. A number of important molecules which absorb in this region include $O_2$, HBr , HCl, HF, HI, $C_6H_6$, $NO_2$, $H_2O_2$, $NH_3$, $C_2H_2$, HCN, CO, $CO_2$, $H_2O$, $CH_4$, NO.

Absorptions in the near IR region are due to overtone and combination bands which are two to three orders of magnitude weaker than fundamental band absorptions. But, thanks to the high quality and power of these lasers, some of the loss of sensitivity due to the weak absorption coefficients can be regained by the use of high frequency modulation (FM) techniques. The sensitivities achievable for these instruments are in the part per million.m range, about 1% to 10% of the sensitivities attainable with the more complex mid-IR systems and which is more than adequate for most commercial and regulatory requirements. The use of FM modulation techniques also permit the use of RF components which enable construction of instruments which are much smaller, lighter and less expensive than those using wavelength modulation.

## 2. THE LASAIR SYSTEMS

Unisearch has now developed the LASAIR series of instruments based on these near infrared laser diodes. There are three versions of this instrument: The LASAIR-R uses a retroflector for remote sensing, the LASAIR-S uses fiber optics for in-stack monitoring and the LASAIR-P is a point monitoring instrument.

A schematic view of the remote sensing LASAIR-R is shown in Figure 1. The diode laser is housed in a thermoelectrically-cooled unit for temperature control and tuning. Most of the laser beam is directed to a transmission mirror, while a small fraction is directed through a cell containing the gas of interest to a separate reference detector which is used to lock the instrument to the desired line and also serves as an internal calibration standard. The main beam is launched by the transmission steering mirror to the retroreflector which can be located from 1 to 1000 meters away. The reflected beam is collected by a small, 10 cm Cassegrain telescope and focused to the primary detector. The eyepiece is used to acquire the target for initial set-up with the laser turned off. The eyepiece can also be used to receive part of the focused beam to auto align the system. The drive mechanism can be motor-operated to acquire any individual and multiple targets, automatically, if desired, using a seeking program. Being a laser source, the acquisition of the target is very straight-forward

The application of the LASAIR-R on-road, remote sensing measurements of auto exhausts is described in detail in another presentation at this symposium. Figure 2 shows the results measurements of the $CO/CO_2$ ratio of the exhaust from a test vehicle operating at the Ford Motor

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Company's test track at Dearborn MI. The fully-instrumented test vehicle was equipped with an on-board FTIR capable of acquiring time-resolved emissions of thirty exhaust components simultaneously, including CO and $CO_2$. The test vehicle was operated under a variety of conditions including changing air-to-fuel ratios. The LASAIR-R measured the ratio in the plume immediately after the vehicle passed with a time resolution of 0.01 s and averaged the data for ~0.5 sec which was the period during which the plume was measurable at the test point. The on board FTIR measured the $CO/CO_2$ ratio continuously throughout the drive by and provided an average value for the ratio. The agreement between the two sets of measurements was very good and the operators commented on the ease with which the LASAIR-R was set up and operated.

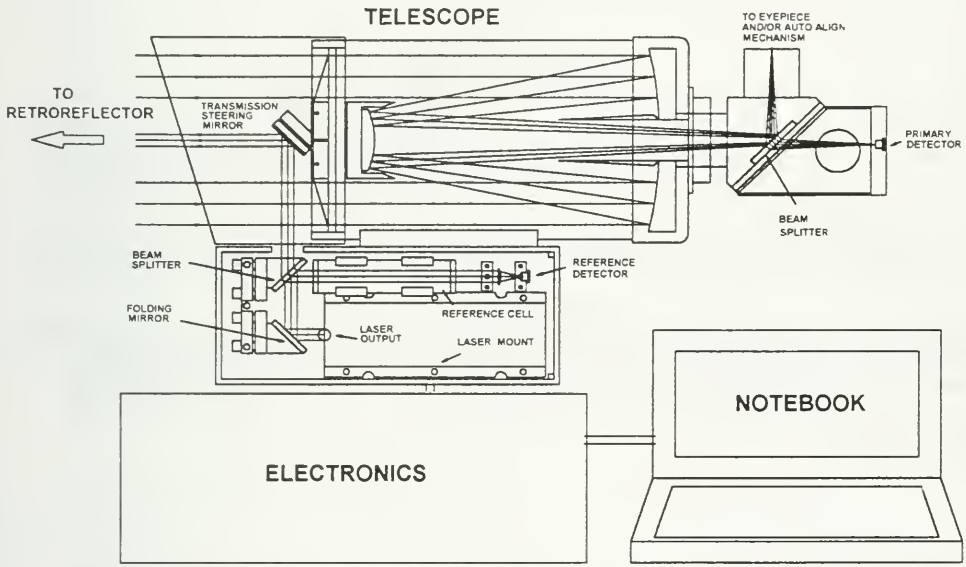


**FIGURE 1**: Schematic of the remote sensing system - LASAIR

The second version of the system is the LASAIR-S designed for continuous emission monitoring and process control. The diode laser and detector are both mounted in a control unit at some suitable location inside the plant. The laser beam is then transmitted to the stack by fiber optics, launched across the stack and returned to the detector by fiber optics. Two options are available for transmission across the stack. One is an open path with the launching optics and the retroflector offset from the stack to prevent exposure to the exhaust gases and temperature. The other is a mobile and self-supporting 1.50 m probe shown schematically in figure 3. The probe consists of a perforated tube terminating with a retroflector at one end the optical fibers at the other end along with appropriate optics for launching and receiving the beam. Clean air is continuously blown into the retroflector and OAP chambers and a cell is located in the main tube for calibration purposes. Clean air is flowed through the cell to which known flows of calibrating gas can be added when desired to provide calibration at the stack temperature and pressure. The probe provides two meters of analytical path and is suited for moderate to high concentration monitoring. Since all the optical components are

mounted on the same base continuous alignment is assured and the probe can be readily removed and installed elsewhere within the stack/duct complex.

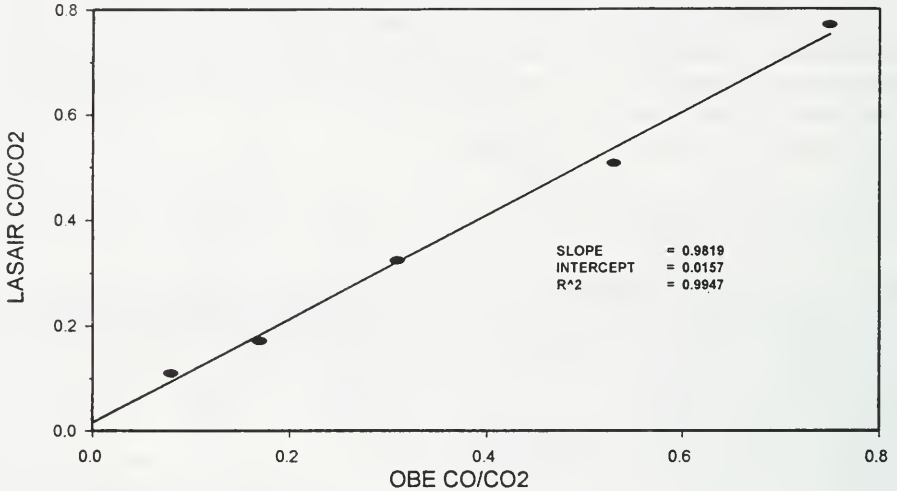


**FIGURE 2:** Comparison of the $CO/CO_2$ ratio measured by the LASAIR with the on-board FTIR $CO/CO_2$ taken on the Ford Motor Company Test Track at Dearborn, MI The speed was set to 30 mph and lambda was varied between 0.80 and 1.0. Data obtained at 10 Hz has been averaged over the time (~0.5 sec) during which the exhaust plume impacted the measurement path.

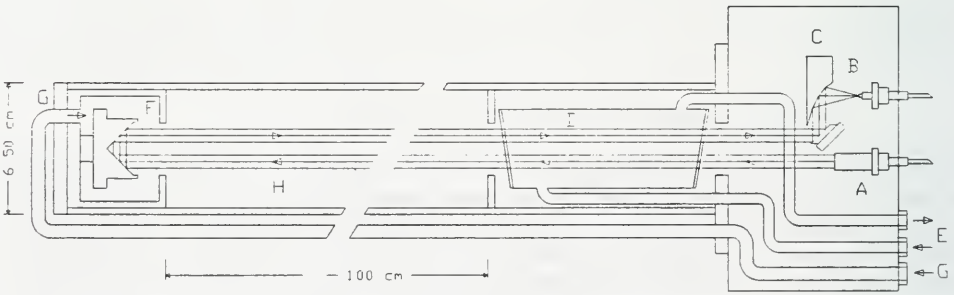


**FIGURE 3**: Fiber optic coupled remote sensing probe

A. Single mode fiber from laser with collimating optics
B. Multimode fiber to detector
C. Off-axis parabolic mirrors
D. Flow through calibration cell
E. Gas inlet and exhaust ports to calibration cell
F. Retroreflector
G. Cooling and cleaning air flow
H. Probe sampling region

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The third version of the instrument, the LASAIR -P is a point monitoring instrument, containing a small, 0.40 m base path White cell in the same control box to provide a total path length of 12m. the appropriate inlet and outlet plumbing is, of course, provided.

## 3. CONCLUSION

We believe that these three near infrared TDLAS systems will fill an important niche where certain gases need to be monitored with high specificity and moderate sensitivity. The ease of operation and the relatively low cost should make it an attractive method for industrial and regulatory markets.

## 4. REFERENCES


1. Mackay, G.I., Karecki, D.R., and Schiff, H.I. "Tunable Diode Laser Absorption Measurements of $H_2O_2$ and HCHO during Mauna Loa Photochemistry Experiment II" in Optical Methods in Atmospheric Chemistry (H.I. Schiff and U. Platt, Eds.) SPIE, 1715, 126-137.

2. Mackay, G.I., Mayne, L.K., and Schiff, H.I., "Measurements of $H_2O_2$ and HCHO by Tunable Diode Laser Absorption during the 1986 Carbonaceous Species Methods Comparison Study in Glendora, California", Aerosol Sci. Technol. 12, 56-63 (1990)

3. Carduner, K.R., Colvin, A.D., Leong, R.Y., Scheutzle, D., Mackay, G.I., Karecki, D.R., and Schiff H.I. "Use of the Tunable Diode Laser to the Real Time Analysis of Engine Oil Economy" Environ, Sci. Tech., 26, 930-934 (1992)



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Unisearch has now developed the LASAIR series of instruments based on these near infrared laser diodes. There are three versions of this instrument: The LASAIR-R uses a retroflector for remote sensing, the LASAIR-S uses fiber optics for in-stack monitoring and the LASAIR-P is a point monitoring instrument.

A schematic view of the remote sensing LASAIR-R is shown in Figure 1. The diode laser is housed in a thermoelectrically-cooled unit for temperature control and tuning. Most of the laser beam is directed to a transmission mirror, while a small fraction is directed through a cell containing the gas of interest to a separate reference detector which is used to lock the instrument to the desired line and also serves as an internal calibration standard. The main beam is launched by the transmission steering mirror to the retroreflector which can be located from 1 to 1000 meters away. The reflected beam is collected by a small, 10 cm Cassegrain telescope and focused to the primary detector. The eyepiece is used to acquire the target for initial set-up with the laser turned off. The eyepiece can also be used to receive part of the focused beam to auto align the system. The drive mechanism can be motor-operated to acquire any individual and multiple targets, automatically, if desired, using a seeking program. Being a laser source, the acquisition of the target is very straight-forward

The application of the LASAIR-R on-road, remote sensing measurements of auto exhausts is described in detail in another presentation at this symposium. Figure 2 shows the results measurements of the $CO/CO_2$ ratio of the exhaust from a test vehicle operating at the Ford Motor

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Company's test track at Dearborn MI. The fully-instrumented test vehicle was equipped with an on-board FTIR capable of acquiring time-resolved emissions of thirty exhaust components simultaneously, including CO and $CO_2$. The test vehicle was operated under a variety of conditions including changing air-to-fuel ratios. The LASAIR-R measured the ratio in the plume immediately after the vehicle passed with a time resolution of 0.01 s and averaged the data for ~0.5 sec which was the period during which the plume was measurable at the test point. The on board FTIR measured the $CO/CO_2$ ratio continuously throughout the drive by and provided an average value for the ratio. The agreement between the two sets of measurements was very good and the operators commented on the ease with which the LASAIR-R was set up and operated.

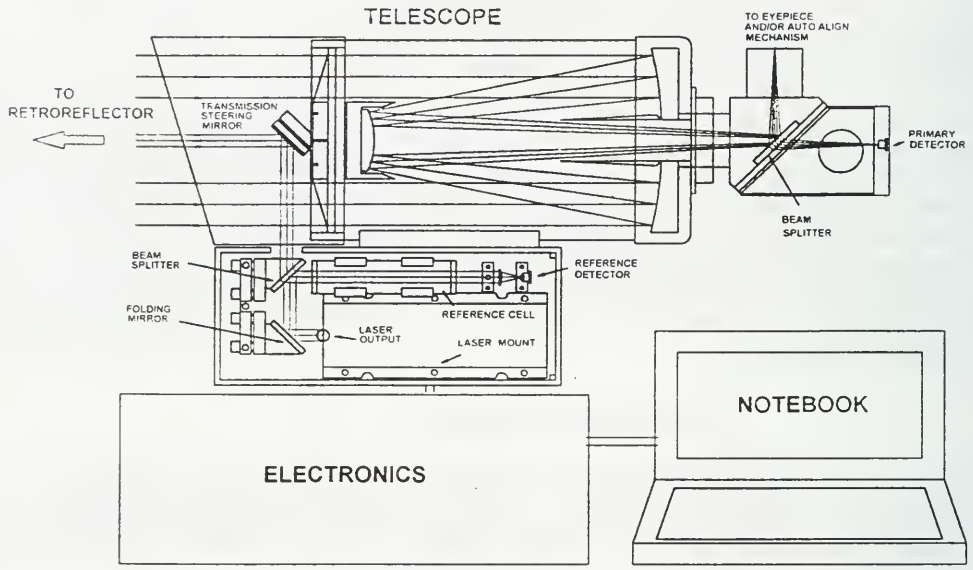


**FIGURE 1**: Schematic of the remote sensing system - LASAIR

The second version of the system is the LASAIR-S designed for continuous emission monitoring and process control. The diode laser and detector are both mounted in a control unit at some suitable location inside the plant. The laser beam is then transmitted to the stack by fiber optics, launched across the stack and returned to the detector by fiber optics. Two options are available for transmission across the stack. One is an open path with the launching optics and the retroflector offset from the stack to prevent exposure to the exhaust gases and temperature. The other is a mobile and self-supporting 1.50 m probe shown schematically in figure 3. The probe consists of a perforated tube terminating with a retroflector at one end the optical fibers at the other end along with appropriate optics for launching and receiving the beam. Clean air is continuously blown into the retroflector and OAP chambers and a cell is located in the main tube for calibration purposes. Clean air is flowed through the cell to which known flows of calibrating gas can be added when desired to provide calibration at the stack temperature and pressure. The probe provides two meters of analytical path and is suited for moderate to high concentration monitoring. Since all the optical components are

mounted on the same base continuous alignment is assured and the probe can be readily removed and installed elsewhere within the stack/duct complex.

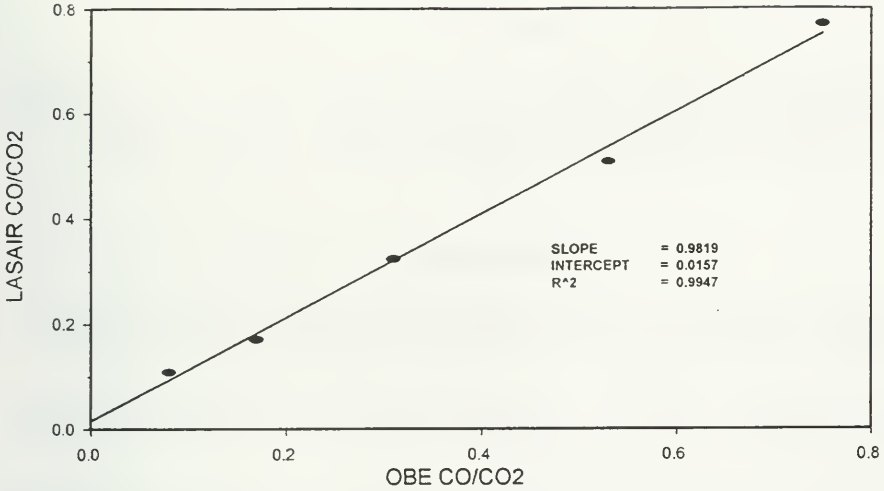


**FIGURE 2:** Comparison of the $CO/CO_2$ ratio measured by the LASAIR with the on-board FTIR $CO/CO_2$ taken on the Ford Motor Company Test Track at Dearborn, MI The speed was set to 30 mph and lambda was varied between 0.80 and 1.0. Data obtained at 10 Hz has been averaged over the time (~0.5 sec) during which the exhaust plume impacted the measurement path.

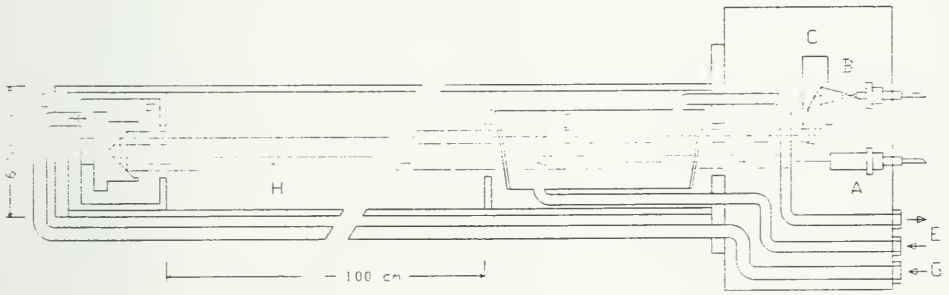


**FIGURE 3**: Fiber optic coupled remote sensing probe

A. Single mode fiber from laser with collimating optics
B. Multimode fiber to detector
C. Off-axis parabolic mirrors
D. Flow through calibration cell
E. Gas inlet and exhaust ports to calibration cell
F. Retroreflector
G. Cooling and cleaning air flow
H. Probe sampling region

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The third version of the instrument, the LASAIR -P is a point monitoring instrument, containing a small, 0.40 m base path White cell in the same control box to provide a total path length of 12m. the appropriate inlet and outlet plumbing is, of course, provided.

## 3. CONCLUSION

We believe that these three near infrared TDLAS systems will fill an important niche where certain gases need to be monitored with high specificity and moderate sensitivity. The ease of operation and the relatively low cost should make it an attractive method for industrial and regulatory markets.

## 4. REFERENCES


1. Mackay, G.I., Karecki, D.R., and Schiff, H.I. "Tunable Diode Laser Absorption Measurements of $H_2O_2$ and HCHO during Mauna Loa Photochemistry Experiment II" in Optical Methods in Atmospheric Chemistry (H.I. Schiff and U. Platt, Eds.) SPIE, 1715, 126-137.

2. Mackay, G.I., Mayne, L.K., and Schiff, H.I., "Measurements of $H_2O_2$ and HCHO by Tunable Diode Laser Absorption during the 1986 Carbonaceous Species Methods Comparison Study in Glendora, California", Aerosol Sci. Technol. 12, 56-63 (1990)

3. Carduner, K.R., Colvin, A.D., Leong, R.Y., Scheutzle, D., Mackay, G.I., Karecki, D.R., and Schiff H.I. "Use of the Tunable Diode Laser to the Real Time Analysis of Engine Oil Economy" Environ, Sci. Tech., 26, 930-934 (1992)



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